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EFFECT OF DIFFERENT SOIL TREATMENTS ON MICROBIAL ACTIVITY AND AVAILABILITY OF MANGANESE IN MANGANESE DEFICIENT SOIL[1]

M. I. TIMONIN AND G. R. GILES[2]

WITH ONE PLATE

SOIL is an extremely complex natural formation which originated and developed as a result of the interaction of many factors. In the study of these factors many independent sciences have contributed such as geology, mineralogy, chemistry, physics, botany, meteorology, climatology, microbiology, and others. Detailed investigation of soil, therefore, cannot be made without close contact with these sciences.

During the last 50 years the close co-operation of soil science with microbiology and chemistry has resulted in the appreciation of the importance of the so-called 'minor elements', a group of great theoretical as well as practical significance. Among the minor elements manganese is regarded as essential with respect to its practical application in agriculture. The value of manganese in nature has been established by several investigators who have concluded that this element performs a most important function in living organisms and consequently is indispensable for their normal development.

In the soil, manganese exists as manganese oxide of varying degrees of oxidation. From the point of view of the availability to the plant, these oxides may be subdivided into three basic forms: (*a*) manganese oxide which is readily available to the plant; (*b*) the hydrated form which is not readily available but becomes available with changes in the physical conditions of the soil; (*c*) a difficultly available form which becomes available only after drastic changes in the soil. From the practical point of view it is important to know in what state of oxidation manganese exists in the soil.

It is known that certain soils contain enormous numbers of small, sometimes microscopic, 'concretions'. These concretions prove to be a mineral form of manganese, such as psilomelane, sometimes in crystalline form, but in the majority of cases in the amorphous state, and as 'wads'—amorphous hydrated forms of manganese oxides. At the present time there is no direct explanation of the kind of chemical reaction which takes place in the soil that cleanses manganese from impurities and deposits it in a concentrated form. However, it is suggested that two phenomena play an important role in this process, namely, living matter and the ground water which envelops the individual soil particles and under the effect of certain physiochemical laws acts as a thermodynamic membrane. Microbial activities are also localized in this aqueous membrane.

In many instances it can be definitely stated that the formation of the

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mangano-ferruginous concretions is a result of microbial activity. Thus Schorler (Waksman, 1932) reported that threads of *Crenotrix polyspora* contain 6–9 per cent. of iron and 30–60 per cent. of MnO_2. Beijerinck (1913) described a bacterium which obtains its necessary energy from the oxidation of manganese oxide into a manganic oxide. Thiel (1925), furthermore, described several species of fungi which were able to accumulate up to 12 per cent. of manganese in the mycelium. Algae and liverworts contain up to 1 per cent. of manganese in their tissues. Leeper (1935) observed the biological oxidation as well as the reduction of manganese in the soil. Mann and Quastel (1946) attributed the oxidation of manganese entirely to biological means. Kalinenko (1946) demonstrated the formation of ferro-manganic concretions by means of bacteria. In Canada, McLachlan (1941) and Chaplin (1946) attributed the deficiency of manganese in certain soils to microbial activity.

A review of the literature points to the fact that soil micro-organisms play, if not a major, certainly an important role in the processes of the oxidation of manganese in the soil. Our own results (Timonin, 1946) obtained under field conditions indicate that the application of soil fumigants such as cyanogas, $Ca(CN)_2$, chloropicrin, formaldehyde, and carbon bisulphide reduced the population of manganese-oxidizing, cellulose-decomposing, and denitrifying bacteria in the soil.

Experimental Procedure

The soil for experimental purposes was obtained from a manganese-deficient area and sixteen 3-gallon pots were potted with this soil and divided into four lots, each lot receiving the following treatments:

1. $MnSO4{\cdot}7H_2O$ (100 lb./acre).
2. $Ca(CN)_2$ (500 lb./acre).
3. Straw mulch (2 in. thick).
4. Control (untreated soil).

Therefore this plan furnished four replicates of each treatment. Manganese sulphate was mixed with the soil prior to potting. For the application of cyanogas[1] a hole in the centre of the pot was drilled by means of an iron rod, $\frac{1}{2}$ in. in diameter, through the entire depth of the soil, and cyanogas at the rate of 500 lb. per 2,000,000 lb. of soil was placed in each hole, which was then filled up with loose soil. Pots were then weighed and the moisture content of the soil was brought up by addition of distilled water to 50 per cent. of the total moisture-holding capacity which was maintained throughout the experiment.

Numbers of the different micro-organisms were estimated by plating or dilution methods. Each of four replicates of the treatment was analysed separately and each dilution was poured into four plates. Thus the numbers presented in this paper are the arithmetical means of sixteen counts. Soil extract agar of pH 6·8–7·0 and 3·8–4·0 was used for total counts of bacteria and actinomycetes and fungi respectively, spore-forming bacteria being estimated on plates poured from dilutions after heating to 80° C. for 10 minutes. Casein-hydrolysing bacteria were

[1] Cyanogas G fumigant is a trade name of calcium cyanide, manufactured by American Cyanomid Company, 30 Rockefeller Plaza, New York, N.Y.

counted on milk-agar plates. Manganese-oxidizing organisms were determined on Gerretsen's manganese-citrate agar.

The other groups of organisms were determined by dilution method with appropriate selective liquid media, using two tubes for each dilution. Thus the numbers of these groups of organisms presented in this paper are the arithmetical means of eight counts, which had been corrected by the application of McCrady's tables. Cellulose-decomposing bacteria were estimated in Omeliansky's medium, nitrifying bacteria in Winogradsky's medium, and denitrifying bacteria in Giltay's solution.

Samples of soil for microbiological analysis were taken 5, 10, 15, 44, 101, 136, 185, 248, and 342 days after treatment, while those for chemical analysis were taken on the 15th day.

In the chemical investigation of the soil samples three forms of active manganese were determined, namely, water-soluble, replaceable, and easily reducible, as outlined by Sherman, McHargue, and Hodgkiss (1942). For the determination of water-soluble manganese a sample of the soil was removed from the pot and immediately extracted with distilled water, using a soil : water ratio of 1 : 5 on a moisture-free basis. Replaceable manganese was determined on another sample of soil by immediate extraction with normal neutral ammonium acetate using the same ratio as above. The easily reducible manganese was determined by extracting the residue from the exchangeable manganese extraction with normal neutral ammonium acetate containing 0·2 per cent. hydroquinone.

The manganese from the above soil extractions was determined according to the Willard and Greathouse (1917) method of oxidation with potassium periodate. The colour intensity was read on a Klett-Summerson photo-electric colorimeter using a No. 54 green filter. The hydrogen-ion concentration was determined by means of a glass-electrode pH meter in 1 : 2·5 soil suspension in distilled water.

Each of four replicates of each treatment was analysed separately, and the data recorded herewith are the arithmetical means of four determinations of each sampling.

Results

Effect of different treatments on microbial activity

From the data presented in Tables 1 and 2 and illustrated by Figs. 1, 2, and 3 it is apparent that the application of calcium cyanide enhanced the activity of bacteria to three times that of control soil 5 days after treatment, but on consecutive sampling the counts indicated a sharp decrease in numbers. However, on the average, counts were still somewhat higher than in the control soil. Application of manganese sulphate and straw mulch had very little effect on the total number of bacteria. Fungi, on the other hand, were depressed in the early stage of the experiment by cyanogas and stimulated by manganese sulphate. The effect of straw mulch resulted in higher counts of fungi at the later stage of the experiment. Actinomycetes were not appreciably affected by treatments. Counts of nitrifying, casein-hydrolysing, and spore-forming bacteria

also were not affected by the treatments used and for this reason were not included in the tables.

TABLE 1

Influence of Different Treatments upon Abundance of Micro-organisms in the Soil

Treatment	Days of incubation					
	5	10	15	44	248	342
	Bacteria*					
$MnSO_4$	64	83	86	66	49	14
Cyanogas	209	63	71	77	79	13
Mulch	70	95	80	76	56	19
Control	64	89	76	49	42	14
	Actinomycetes*					
$MnSO_4$	6	12	10	7	7	..
Cyanogas	17	9	10	8	7	..
Mulch	8	9	8	6	8	..
Control	8	9	7	5	7	..
	Fungi*					
$MnSO_4$	37	58	40	33	..	44
Cyanogas	20	13	29	27	..	46
Mulch	36	58	45	104	..	49
Control	31	30	30	23	..	41

* Bacteria and actinomycetes in millions, fungi in thousands per g. moisture-free soil.

TABLE 2

Calculated Least Significant Difference (= 0·05) for Micro-organisms and Available Manganese*

Days of incubation	Organisms × 1,000			Available Mn p.p.m.			
	Mn oxid.	Denitrif.	Cell.† decomp.	H_2O sol.	Replace.	Easily reduc.	Total available
5	70	408	33	..	..	..	..
10	46	793	n.s.‡	..	..	..	..
15	81	456	n.s.	n.s.	0·703	0·140	4·344
44	92	216	n.s.	0·015	0·179	3·413	3·749
101	n.s.	n.s.	n.s.	0·006	0·079	3·832	3·607

* Least significant differences were calculated from original data of which figures in Table 2 are averages.

† Counts of cellulose-decomposing bacteria in cyanogas-treated soil were obviously significantly low and were not included in these calculations.

‡ Not significant.

Whereas the total counts of bacteria were only moderately affected by the treatments, the physiological groups of bacteria showed a significant response. Application of manganese sulphate and straw mulch stimulated the activity of manganese-oxidizing, denitrifying, and cellulose-decomposing organisms. Following manganese treatment the activity of

denitrifying bacteria reached the highest point on the 10th day, that of manganese-oxidizing bacteria on the 15th day, and that of cellulose-decomposing bacteria on the 136th day after treatment. A similar effect

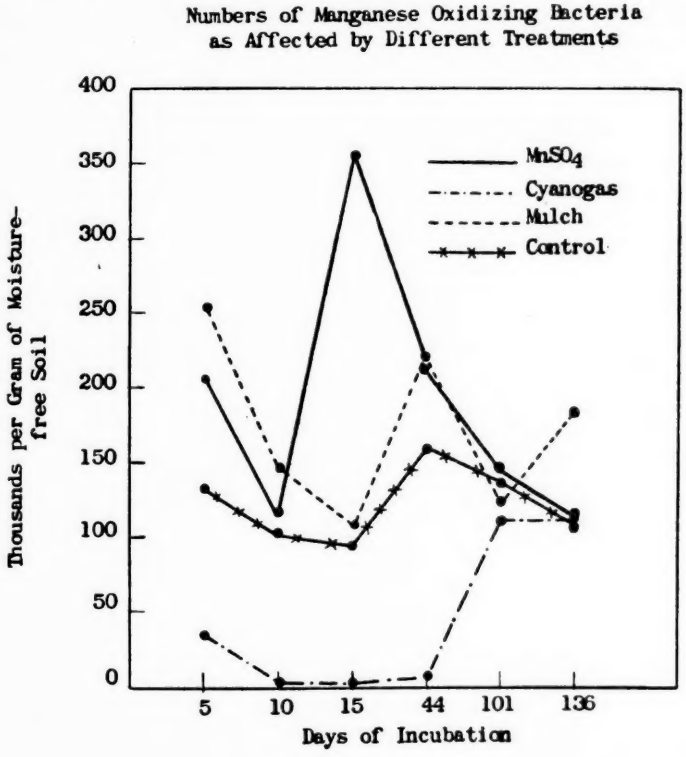

FIG. 1.

was obtained with straw mulch except that cellulose-decomposing and manganese-oxidizing bacteria showed, at the end of the experiment, significantly higher activity than with any other treatment. A high percentage (20 per cent.) of cellulose-decomposing bacteria also proved to be able to oxidize manganese when grown on calcium citrate-manganous sulphate medium.

Interesting results were obtained with cyanogas treatment. Counts of denitrifying and manganese-oxidizing bacteria were significantly lower than with any other treatment used, until somewhere between the 44th and 100th day after treatment. In samples obtained on the 101st day these two groups of organisms showed approximately the same or higher count as compared with the control soil; in other words, they reached the original equilibrium of the untreated soil. Cellulose-decomposing organisms remained significantly low to the end of the experiment. In general

it may be stated that cyanogas showed a selective activity against soil micro-organisms.

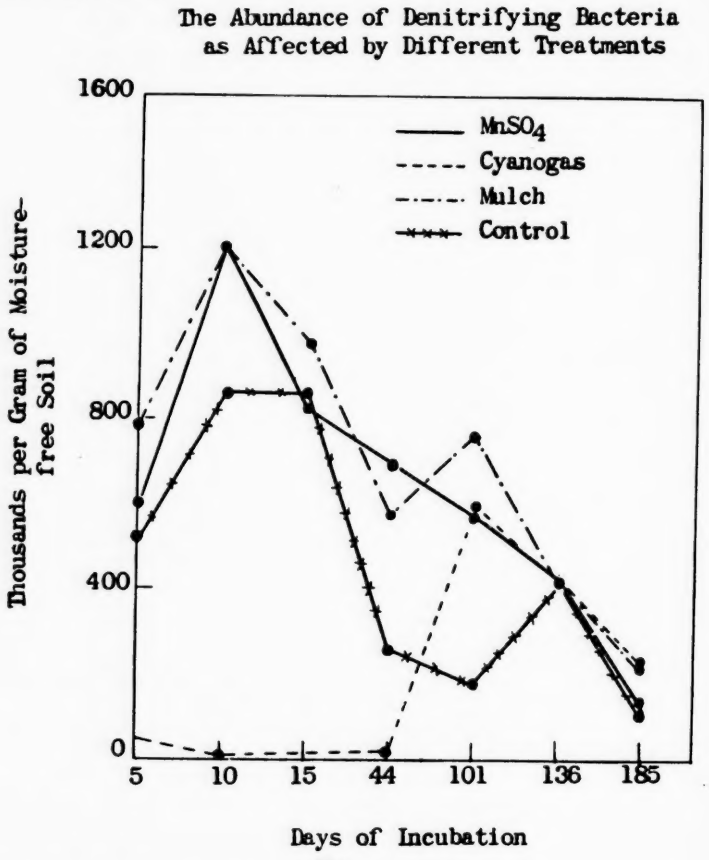

FIG. 2.

Effect of different treatments on the availability of manganese

The data summarized in Figs. 4 and 5 and Table 2 indicate that water-soluble manganese was not affected by the cyanogas, mulch, or manganese treatment. A significant difference, however, was obtained by the application of manganese sulphate with respect to easily reducible manganese which remained higher than with any other treatment. Replaceable manganese was significantly higher on the 15th day after treatment, but later showed a sharp decrease and on the 101st day dropped to the same level as that in the mulch treatment or control soil. Except on the 15th day of sampling the cyanogas treatment resulted in a significantly higher content of replaceable manganese than in the soils receiving other treatments.

Effect of different treatments on an indicator crop

Data presented in Table 2 indicate that numbers of manganese-oxidizing and denitrifying bacteria in the cyanogas-treated soil on the 101st day reached the same level as those in the control soil; thus the effect of cyanogas upon these two groups of organisms had disappeared. However, on the same date the content of replaceable manganese remained higher than with any other treatment.

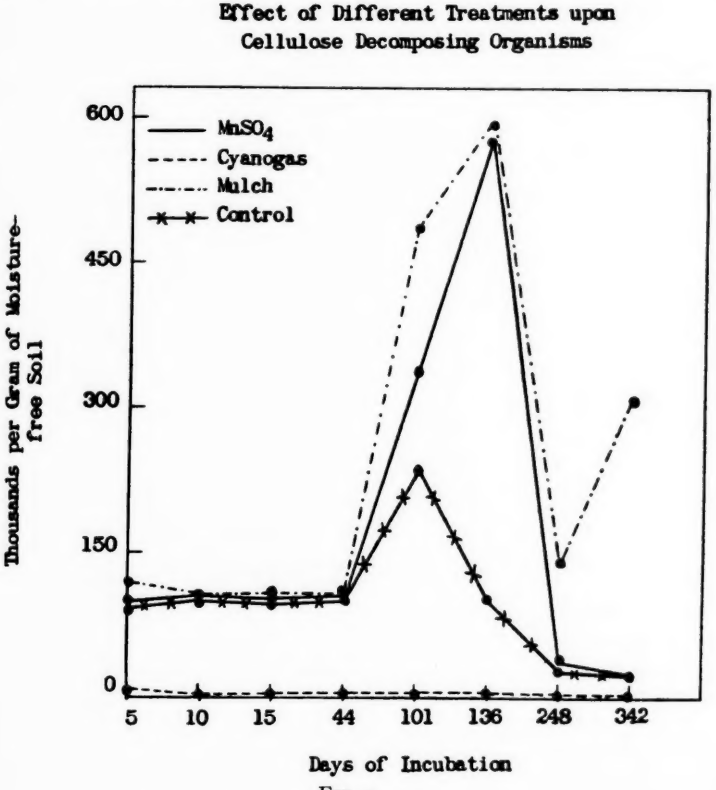

FIG. 3.

To note the effect of these prevailing differences upon the availability of manganese to the growing plant, on the 125th day of the experiment two pots of each treatment were sown with the indicator crop, a variety of oats susceptible to manganese deficiency. Six weeks later plants grown in manganese- and mulch-treated soil, as well as in control soil, developed typical manganese-deficiency symptoms. At the same time plants grown in the cyanogas-treated soil (Plate I) were vigorous and free from symptoms of manganese deficiency. Plants on the manganese-treated soil produced slightly better growth than on control soil, but

symptoms (grey lesions) were as numerous as on the plants of the control soil. Owing to severe manganese deficiency in the mulch-treated soil, by the 6th week after planting only a few seedlings remained alive while the others developed severe symptoms of manganese deficiency and dried up.

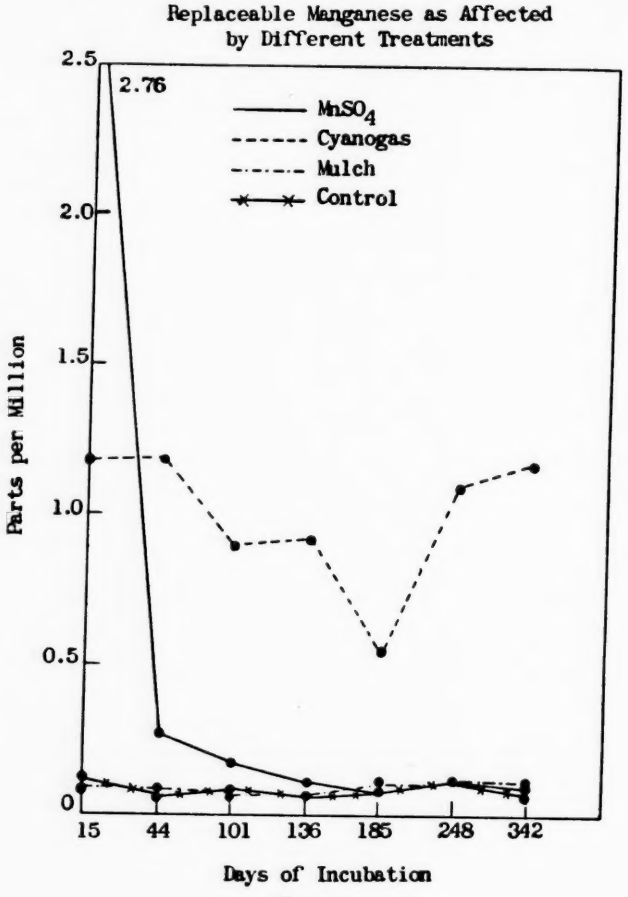

FIG. 4.

Discussion

The results obtained with application of calcium cyanide are in agreement with the statement of Smith *et al.* (1945), indicating that it acted in a similar selective bacteriocidal and bacteriostatic manner as did ammonium thiocyanate. The same treatment resulted in an increase of replaceable manganese, confirming the results obtained by Dalton and

Hurwitz (1948) with hydrocyanic acid and those of Fujimoto and Sherman (1948) with formaldehyde. However, examining the data presented in Figs. 1–5 we notice that on the 101st day the density of manganese-oxidizing and denitrifying organisms in the cyanogas-treated soil was considerably increased while at the same time the content of replaceable

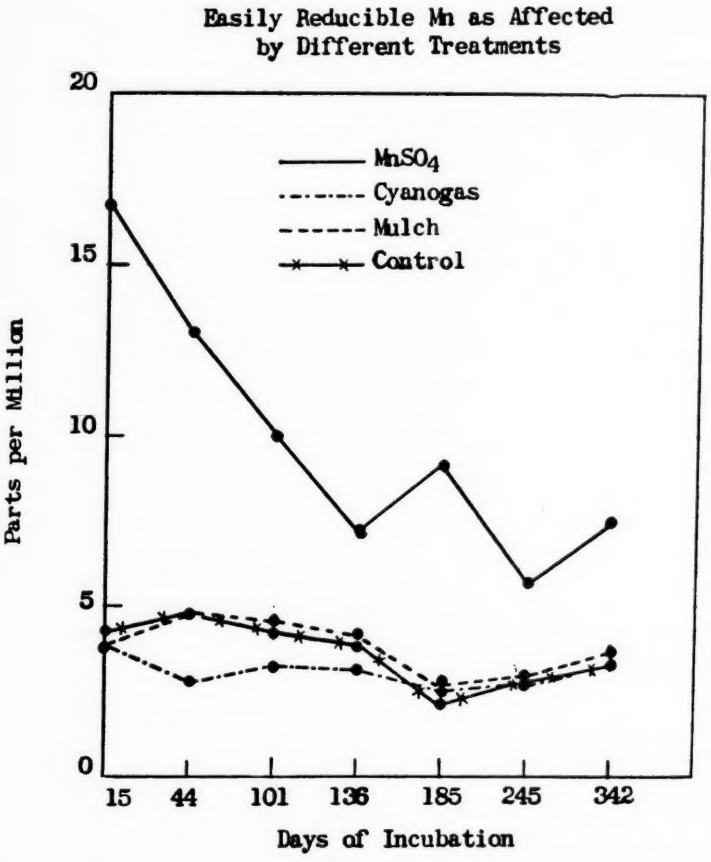

FIG. 5.

manganese decreased. This decrease, therefore, may be attributed to the increased activity of these two groups of organisms. On the other hand, it is quite apparent that at the time of planting of the indicator crop the only difference existing at that time in the calcium-cyanide-treated soil from the other treatments was the slightly higher content of replaceable manganese and the very low count of cellulose-decomposing bacteria. Therefore the indicator crop showed no correlation between the abundance of the manganese-oxidizing and denitrifying bacteria and the

symptoms of manganese deficiency. The only two factors which might be considered as responsible for the correction of manganese deficiency are the high content of replaceable manganese and the low count of cellulose-decomposing bacteria.

If, however, previous results with manganese-sulphate treatment under field conditions are considered (Timonin, 1946) (when the indicator crop was sown on the 13th–14th day after treatment and later developed practically the same severity of manganese-deficiency symptoms as the same crop on the control soil), and compared with the data obtained with the manganese treatment on the 15th day of sampling in the present experiment, it will be apparent that the high content of replaceable manganese in the cyanogas-treated soil is not the only factor responsible for the correction of manganese deficiency, because the content of replaceable manganese in the manganese-treated soil on the 15th day was much higher than in the cyanogas-treated soil. A low count of cellulose-decomposing bacteria, which are also capable of oxidizing manganese, therefore could be regarded as being a factor of importance in the improvement of manganese deficiency in the soil used in this experiment.

The high content of easily reducible manganese in the manganese-treated soil had no corrective effect on manganese deficiency.

Summary

In a study of the effect of different treatments on the microbial activity and the availability of manganese in manganese-deficient soil it was found that the application of cyanogas significantly reduced the density of population of manganese-oxidizing, denitrifying, and cellulose-decomposing organisms. Only on the 101st day after treatment did the manganese-oxidizing and denitrifying organisms reach the same density as that in the soil treated with manganese sulphate, mulch, or in the control soil. The density of cellulose-decomposing organisms remained depressed to the end of the experiment.

Application of manganese sulphate and straw mulch resulted in an increased activity of cellulose-decomposing, denitrifying, and manganese-oxidizing organisms.

Results of chemical analyses indicated that the water-soluble manganese was not affected by the different treatments, but remained practically at the same level throughout the experiment. Replaceable manganese was found to be higher in calcium-cyanide-treated soil than with any other treatments and was still 10 times higher at the end of the experiment. The highest content of easily reducible manganese was found in the manganese-treated soil, and it remained higher than in any other treated soil throughout the experiment.

Analysis of the data of the microbiological tests and of the content of available manganese indicated a negative correlation throughout the experiment between the density of cellulose-decomposing organisms and replaceable manganese, and the same type of correlation was established between the density of manganese-oxidizing and denitrifying organisms and replaceable manganese until the 101st day after treatment.

Effect of treatments on manganese availability (indicator crop of oats)

(1) $MnSO_4$, 100 lb. per acre
(2) Cyanogas, 500 lb. per acre
(3) Straw mulch, 2 in. thick
(4) No treatment

M. I. TIMONIN and G. R. GILES
PLATE I

The indicator crop planted on the 125th day after treatment did not develop the manganese-deficiency symptoms in cyanogas-treated soil. The correction of manganese deficiency in this case, therefore, could be attributed to the high content (0·9 p.p.m.) of replaceable manganese and to the reduced activity of cellulose-decomposing organisms.

A high content (10 p.p.m.) of easily reducible manganese in the manganese-treated soil failed to remedy manganese deficiency.

REFERENCES

BEIJERINCK, M. W. 1913. Folia Microbiologica, **2,** 123.
CHAPLIN, C. E. 1946. Thesis presented to the Faculty of Graduate Studies, McGill University.
DALTON, F. H., and HURWITZ, C. 1948. Soil Sci. **66,** 233.
FUJIMOTO, C. K., and SHERMAN, G. D. 1948. Soil Sci. **66,** 131.
KALINENKO, V. O. 1946. Microbiologiya, **15,** 364.
LEEPER, G. W. 1935. Proc. Roy. Soc. Victoria, **47,** 225.
MANN, P. J. G., and QUASTEL, J. H. 1946. Nature, **158,** 154.
MCLACHLAN, J. D. 1941. Sci. Agric. **22,** 201.
SHERMAN, G. D., MCHARGUE, J. S., and HODGKISS, W. S. 1942. Soil Sci. **54,** 253.
SMITH, N. R., DAWSON, V. T., and WENZEL, M. E. 1945. Soil Sci. Soc. Amer. Proc. **10,** 197.
THIEL, G. A. 1925. Econ. Geol. **20,** 301.
TIMONIN, M. I. 1946. Soil Sci. Soc. Amer. Proc. **11,** 284.
WAKSMAN, S. A. 1932. Principles of Soil Microbiology. Williams and Wilkins Company, Baltimore.
WILLARD, H. H., and GREATHOUSE, L. H. 1917. J. Amer. Chem. Soc. **39,** 2366.

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ALLOPHANE IN VOLCANIC ASH SOILS

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Introduction

WITH ONE PLATE

IN the course of examination of volcanic ash soils from a hospital site at New Plymouth as a foundation for proposed new buildings, and from the sites of hydro-electric stations at Whakamaru and Atiamuri on the Waikato River for earthwork construction, the high water-holding capacity, high shrinkage, and irreversible drying of these soils were very striking. A moderately high compressibility under load was also shown by some of the New Plymouth soils. It is intended to present data in a subsequent paper on the physical properties of these ash soils, but the object of the present investigation is to examine the finer fractions of these soils in order to identify the minerals responsible for the above-mentioned physical properties. The parent material of the soils from the New Plymouth site is largely andesitic, and from the Whakamaru and Atiamuri sites is both andesitic and rhyolitic (Grange, 1931).

Clay fractions were separated from these soils after using the deferration procedure of Dion (1944), and on differential thermal analysis gave curves resembling those published for allophane (Berkelhamer, 1944).

A subsoil sample of heavy clay texture obtained from the site of a proposed hard-standing area at Whenuapai airfield, 13 miles north-west of Auckland City, showed similar physical properties to the andesitic ash soils but had much higher water-content and shrinkage. The parent material of this soil is thought to be water-sorted volcanic ash, and although the rainfall at Whenuapai is lower than at the other sites mentioned, the original swampy nature of the portion of the airfield where the sample was found could account for the ash being in a similar state of weathering. The clay fraction was identified as a fairly pure allophane, practically free of sesquioxides.

Allophane was also found by differential thermal analysis in admixture with kaolin in a heavy clay weathered from the volcanic ash beds at another location on the hospital site in New Plymouth, and in the clay fraction of a soil formed from the rhyolitic Mamaku ash shower on the eastern side of Lake Rotorua, although the clay content of this latter soil was not high enough to have much influence on physical soil properties.

Mr. N. H. Taylor (1933), who had found that the clay fractions prepared by dispersion with water or very dilute NaOH from certain 'waxy pans' occurring in old ash beds found on the Mairoa Plateau, west of Te Kuiti, gave silica-alumina ratios close to 1·0 and were accordingly presumed to be allophane, suggested examination of this material by differential thermal analysis. The 'waxy pan' had similar physical properties to the Whenuapai soil, but the clay fraction separated from it was found to contain appreciable gibbsite as well as allophane. The subsoil of the top ash shower on the Mairoa Plateau resembled the New Plymouth soil and contained mostly allophane and some limonite.

The predominance of allophane in the clay fractions in all these soils and also its probable presence in some silt fractions was later inferred from the largely amorphous nature of the material when examined with a Philips Geiger X-ray spectrometer.

The deferration procedure of Jeffries (1946) was used in preparing clay fractions from the Whenuapai, Mamaku ash, and Mairoa Plateau soils. Allophane was also identified in clay fractions prepared from some of these soils by methods which did not involve deferration.

Preparation of Clay and Silt Fractions

The parent materials and locations of the soil samples used in this work are set out in Table 1, below.

TABLE 1

Origin and Location of Volcanic Ash Soils

Clay or silt sample Nos.	*Ash shower*	*Location*	*Depth from surface*
1 *a–c*	Egmont (andesitic)	New Plymouth Hospital	16–17 ft.
2	Tirau (andesitic+rhyolitic)	Whakamaru Hydro, G18	..
3 *a*	,, ,, ,,	Atiamuri Hydro, Shaft 29	5 ft.
3 *b*	,, ,, ,,	,, ,, Shafts 25 and 26	
4 *a–c*	Mairoa (andesitic+rhyolitic)	Ngapenga Rd., Mairoa	9–15 in.
5	pre-Hamilton	,, ,, ,,	6 ft.
6 *a–c*	Water-sorted ash	Whenuapai airfield	6 ft.
7	Mamaku (rhyolitic)	East side, Lake Rotorua	16 in.

The procedures used in obtaining the clay and silt fractions from the above soils are set out in Table 2.

TABLE 2

Soil Pretreatments and Yields of Clay

Sample No. (see Table 1)	*Treatment*	*Clay %*
1 *a*	Dion deferration, Na_2CO_3 dispersion	6·8
1 *b*	,, ,, ,, ,,	13·8
1 *c*	,, ,, N/500 HCl dispersion	14·0
2	,, ,, Na_2CO_3 dispersion	10·9
3 *a*	,, ,, ,, ,,	7·9
3 *b*	No deferration, N/100 NH_4OH dispersion	11·3
4 *a*	Dion deferration, Na_2CO_3 dispersion	27·0
4 *b*	,, ,, N/500 HCl dispersion	21·2
4 *c*	No deferration, N/500 HCl dispersion	30
5	N/5 HCl leaching, Jeffries deferration, Na_2CO_3 dispersion	*c.* 0·5
6 *a*	Jeffries deferration, Na_2CO_3 dispersion	22·6
6 *b*	,, ,, thrice repeated, Na_2CO_3 dispersion	< 5
6 *c*	No deferration, N/100 NH_4OH dispersion	64
7	,, ,, N/500 HCl dispersion	5

Notes: 1. Undried soil was used as starting material, except in the case of sample 1*a*. Yields are calculated on oven-dry soil basis.

2. The Na_2CO_3 solution had a pH of approximately 8·0.

Discussion on Table 2

The reduced yields with sample 1*a* as compared with 1*b* as a result of oven-drying are due to the irreversible drying effects shown by these soils. Even air-drying renders the soil much less dispersible than in its natural state.

N/500 HCl as a dispersing medium was tried in view of the reports by Davies (1933) and the Imperial Bureau of Soil Science (1933) that a dilute acid caused dispersion of some New Zealand volcanic ash soils when the alkaline media used for mechanical analysis produced flocculation. It can be seen that such treatment did not improve the yields of clay, either with or without deferration, in comparison with the results obtained by deferration followed by sodium carbonate dispersion.

The New Plymouth and Mairoa ash soils would not disperse satisfactorily in an alkaline medium without deferration treatment. The yield of clay in the case of the Whenuapai soil agreed closely with the result of mechanical analysis by the Bouyoucos method using sodium silicate and sodium oxalate as dispersing agents. The decreased yield of clay with this last-mentioned soil as a result of the normal Jeffries deferration and

TABLE 3

Differential Thermal Analysis and X-Ray Diffraction Data

Sample	*Fraction*	*D.T.A. conclusions*	*X-ray conclusions*
1 *b*	Clay	Allophane with 3% kaolin	Mostly amorphous with a little felspar.
1 *b*	Silt	..	Mostly amorphous with some quartz, felspar, and orthoclase.
2	Clay	Allophane with 3% kaolin	Mostly amorphous.
3 *a*	,,	,, ,, 5% quartz	,, ,,
3 *b*	,,	,, ,, 2% quartz	,, ,,
4 *a*	,,	,, ,, 5% kaolin and some limonite	,, ,, with small amounts of kaolin and felspar.
4 *a*	Silt	..	More than 50% quartz with some albite.
4 *c*	Clay	Allophane with a little limonite	..
5	,,	,, ,, much gibbsite and 5% quartz	Some amorphous with much gibbsite.
6 *a*	,,	Allophane with 5% quartz.	Mostly amorphous.
6 *b*	,,	Small amount of quartz and unidentified material with endothermics at 135° and 210° but no exothermics. Allophane absent	,, ,, with small amount of unidentified crystalline material.
6 *c*	,,	Allophane with 3% kaolin and 2% quartz	Mostly amorphous.

Notes: 1. Figures for percentages of minor constituents in the D.T.A. column are estimates only.

2. Quartz was identified in the D.T.A. curves by the normal α–β inversion, although it is possible that it has been missed in some samples, since it has been found in the course of work in this laboratory that some forms of quartz sometimes fail to show this inversion. Small amounts of quartz were less easily detected in the X-ray records.

the still smaller yield following the triple deferration treatment are very probably due to attack on the allophane by the reagents.

The soil, of heavy silt loam texture, which was derived from the pre-Hamilton ash shower (a 'waxy pan') required leaching with N/5 HCl

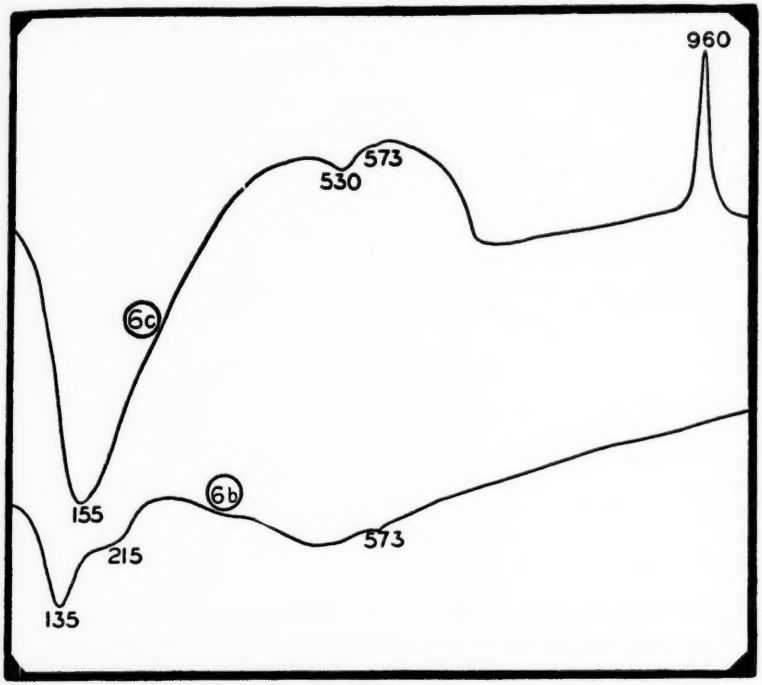

FIG. 1. Differential Thermal Analysis curves for clays containing Allophane
6*c*. (undeferrated) 6*b*. (triply deferrated)

prior to deferration to remove the greater part of the gibbsite present before any dispersion could be effected. The yield of clay was about 5 per cent., and a yield of a similar order was obtained from another sample by heating with N/10 NaOH, followed by dispersion with water only, no deferration treatment being used. This procedure also dissolved some alumina. The low yields of clay from this soil are indicative of only partial dispersion.

The results of differential thermal analysis (D.T.A.) and X-ray diffraction measurements on various clay and silt preparations as detailed in Table 2, are given in Table 3, page 158.

The D.T.A. curves for deferrated and non-deferrated samples were similar, with the important exception that the Whenuapai clay fraction sample 6*b* which had been subjected to the triple deferration showed the absence of the characteristic exothermic peak at about 960° and the initial endothermic low-temperature water-loss effect was much reduced (see Fig. 1). Normal deferration treatment as prescribed by Dion or Jeffries

may apparently not prevent the identification of allophane from the D.T.A. curves, but this mineral may fail to be detected if the treatment should be unduly prolonged. In this connexion it is to be noted that a sample of the 'waxy pan' which was deferrated once by Jeffries's method, but from which the clay fraction was not subsequently separated, behaved on thermal analysis in a similar way to sample 6*b* clay fraction. Reference is made to this 'waxy pan' sample in the later section on dye-adsorption. It seems desirable, therefore, that when seeking to identify allophane in soils, clay fractions should be prepared where possible by methods which do not involve deferration.

The fact that allophane appears amorphous to X-rays suggests that its particle size is below 100 Å. A specimen of what was considered to represent true allophane from Whenuapai, sample 6*c*, was sent to H. L. Nixon of Rothamsted Experimental Station, who has kindly supplied the electron micrograph reproduced in Fig. 2. The smallest particles show no external regularity and are 50 Å or less in equivalent diameter. The larger particles appear to be aggregates.

Chemical Analyses of Clay and Silt Fractions

The results of chemical analyses made of the clay prepared in the course of this investigation are shown in Table 4, the sample numbers being the same as in the previous tables.

It will be seen that the clay fraction samples 3*b*, 4*c*, and 6*c* which have not been deferrated have lower silica-alumina ratios than the samples from the same soil which have been so treated. There is therefore a relative loss of alumina by deferration which becomes almost complete in the triply deferrated sample 6*b*. The excess silica in the deferrated samples is apparently not detectable by thermal analysis.

The low silica-alumina ratio of sample 5 is due to the high gibbsite content. Another clay fraction from the same soil which had more leaching with N/5 HCl before dispersion gave a silica alumina ratio of 0·99.

Because both the Dion and Jeffries deferration treatments involve heating the samples with slightly acid solutions, some attack on the allophane is to be expected, inasmuch as the decomposition of this mineral by fairly concentrated acid has been observed by several investigators. With the majority of clay minerals the effect of deferration on composition should be slight, although Williams (1950) has reported that the Jeffries method gives appreciable losses of alumina and considerable loss of iron from biotite.

The silica-alumina ratios for allophane specimens reported by other workers cover a considerable range. Ross and Kerr (1934) refer to twelve analyses where this ratio varied from 0·74 to 1·98, about one-half being not far from 1·0. Salmang is reported (Pask and Davies, 1943) as recording compositions for the mineral covering the range Al_2O_3, 0·3–1·3 SiO_2, 1·8–8·5 H_2O. Some still more recent analyses (1936, 1948) give silica-alumina ratios between 1·0 and 1·29, with water-contents somewhat over 30 per cent. These specimens, with the possible exception of those described by Salmang, whose monograph was not available, are

from sources other than soil clays. That the silica-alumina ratio for allophane derived from N.Z. volcanic ash soils may show a fairly wide range even without deferration is shown by the analysis of samples *3b*, *4c*, and *6c* (Table 4), bearing in mind that any other constituents are present in only a very small amount.

TABLE 4

Analyses of Clay Fractions of Soils Extracted According to Treatments in Table 2

Sample No.	*1b*	*2*	*3a*	*3b*	*4a*	*4b*	*4c*	*5*	*6a*	*6b*	*6c*
SiO_2 . .	47·17	52·81	50·31	43·5	40·91	43·04	29·33	22·64	44·21	90·29	41·24
Al_2O_3 . .	43·24	37·04	39·32	41·7	43·41	42·33	49·36	70·26	45·73	5·01	57·71
Fe_2O_3 . .	5·27	5·45	4·82	9·5	8·29	8·36	18·40	2·36	0·63	0·62	0·72
TiO_2 . .	0·74	0·47	0·49	0·9	1·55	1·45	1·72	0·93	0·45	0·91	0·49
CaO . .	tr.	tr.	tr.	tr.	tr.	tr.	tr.	n.d.	nil	nil	nil
MgO . .	0·28	0·66	0·48	nil	0·62	0·64	tr.	0·65	n.d.	nil	nil
Na_2O . .	2·38	3·04	n.d.	n.d.	4·57	n.d.	0·69	n.d.	n.d.	1·71	0·15
K_2O . .	0·46	n.d.	n.d.	n.d.	0·62	n.d.	0·29	n.d.	n.d.	0·05	nil
P_2O_5 . .	0·35	n.d.	n.d.	n.d.	0·21	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Total constituents determined .	99·89	99·56	95·42	95·6	100·02	95·82	99·79	96·84	91·03	98·59	100·31
SiO_2/R_2O_3 .	1·73	2·22	2·02	1·55	1·44	1·53	0·82	0·54	1·64	28·4	1·20
SiO_2/Al_2O_3 .	1·85	2·42	2·17	1·78	1·61	1·73	1·01	0·55	1·64	30·6	1·21
Ignition loss*	21·2	15·02	19·7	24·8	24·7	22·05	30·8	27·0	24·0	9·42	31·5
S. G. . .	2·11	2·30	2·21	n.d.	2·10	n.d.	n.d.	n.d.	2·37	n.d.	1·98

* Expressed as percentage of weight of sample dried at 105° C.

Refractive index determination on the clay fraction of sample *6c* by Mr. A. Steiner of the N.Z. Geological Survey gave 1·483, which is close to the average value of 1·480 reported by Ross and Kerr (1934) for specimens of allophane from seven localities.

Base-Exchange Capacity of Allophane

Table 4 shows in several instances deferrated clay fractions containing an appreciable amount of sodium and smaller amounts of potash. Sodium chloride having been added as saturated solution to flocculate the clay suspension, the removal of chloride ion from the clay by washing first with 80 per cent. alcohol followed by 90 per cent. alcohol was taken as freeing it from all alkali salts. Although allophane has been stated to have a low base-exchange capacity, the relatively high alkali content of these clays resulting from the treatment with alkali tartrates or oxalates would be expected to arise by some reaction which is at least analogous to the base-exchange reactions of the crystalline clay minerals. Confirmation of the high capacity of allophane to take up alkali metals was obtained by leaching some of the deferrated clay and silt fractions with neutral potassium acetate solution, removing excess of this salt with alcohol, and determining by flame photometer the potassium which could be subsequently leached out by ammonium acetate solution.

Some soda plus potash contents of the soil fractions have been calculated as milli-equivalents per cent. on the oven-dry basis and tabulated in Table 5 together with the figures for potassium taken up from neutral potassium acetate solution by the same soil fraction.

TABLE 5

Alkali Content of Deferrated Clay Fractions and Potassium taken up from Neutral N Potassium Acetate

Sample	*Fraction*	*Soda plus potash from fusion analysis (m.e. %)*	*Adsorbed potassium (m.e. %)*
1 *b*	Clay	61	75
2	,,	Na_2O only = 82	74
3 *a*	,,	n.d.	96
4 *a*	,,	121	78

Sufficient of preparation 1*b* clay fraction was available for a single determination of base-exchange capacity and total bases by the standard soil method using neutral N ammonium acetate. With the other preparations only sufficient material was left over for determining adsorbed potassium by the flame photometer method. Results by the ammonium acetate method were base-exchange capacity 54 m.e. per cent., total bases 36·5 m.e. per cent., of which 34·7 m.e. per cent. was sodium.

The alkalies in the allophane clays which had been deferrated appear to be rather more loosely held than is the case with exchangeable bases held by other clay minerals. Leaching with distilled water (0·5 g. sample to 250 c.c.) removed about one-half of the total sodium, but a smaller proportion of potassium from the clay fractions. The remainder of the sodium and most of the potash could be leached out with 250 c.c. neutral N ammonium acetate.

These indications of high base-exchange capacity for allophane are comparable with the values of base-exchange capacity towards 0·5 neutral N barium acetate, found by Mattson for iso-electrically precipitated aluminium 'silicates' of similar chemical composition to the clay fractions described above.

Mattson (1931) states that a precipitate of the composition $Al_2O_3(SiO_2)$ 1·63 took up 47 m.e. per cent. Ba while another corresponding to the composition $Al_2O_3(SiO_2)$ 1·09 had a base-exchange capacity measured in the same way of 30 m.e. per cent.

Further work on the whole soil from Whenuapai has shown that the base-exchange capacity as determined with neutral N/2 barium acetate is somewhat higher than the values found using N potassium or ammonium acetate, but is still within the order of the results given in Table 5.

Adsorption by Allophane of Alizarin Red S

Hardy and Rodrigues (1939) have described a method for the estimation of gibbsite alumina in tropical soils by using the adsorptive power of the ignited mineral for the acidic dye Alizarin Red S. When this method was used for quantitative determination of the gibbsite present in some of the soil fractions where it had been clearly detected by D.T.A. and X-ray analysis, it was found that amounts of this mineral were indicated far in excess of that estimated to be present by the two last-mentioned methods. Tests on clay fractions of the Whenuapai soil which appears from the evidence given earlier to be practically pure allophane

showed that this mineral was also capable of adsorbing the dye after ignition under the conditions specified by Hardy in his method. The adsorptive power of ignited allophane is about 70 per cent. of that of ignited gibbsite. Table 6 gives the results of some tests made on volcanic ash soils with this method.

TABLE 6

Adsorption Tests with Alizarin Red S

Sample	*Gibbsite content by dye adsorption*		*Gibbsite content estimated from D.T.A.*	*Minerals present*	SiO_2/Al_2O_3
	Oven-dry material	*Ignited material*			
Whenuapai clay 6c	25	69	nil	Allophane about 95%	1·21
Whenuapai whole soil	35	72	n.d.	Mostly allophane	1·52
Ngapenga Rd., Mairoa, 6 ft. whole soil (cf. No. 5, Table 1)	51	81	10–20	Allophane + 10% gibbsite + 1% kaolin, + 10% silica,	1·13
Ditto but deferrated	n.d.	1·8	2–5	2% gibbsite, 3% kaolin, 25% silica, no allophane.	13·3

It is to be noted that the difference between the gibbsite contents of the Whenuapai clay and the Ngapenga Road soil as measured by dye adsorption is approximately equal to the actual gibbsite content of the latter soil as estimated from the D.T.A. curves.

The deferrated Ngapenga Road soil is comparable with the triply deferrated Whenuapai clay fraction 6*a* in its D.T.A. curve (see Fig. 1), and the silica-alumina ratio in Table 6 confirms that the allophane has been largely decomposed. Decomposition of the allophane has largely destroyed the dye-adsorptive power.

The conclusion to be drawn is that this dye adsorption test for gibbsite must be used with caution when allophane is known to be present in soils.

Dispersion of Soils containing Allophane and Free Sesquioxides

The difficulties in dispersing some volcanic ash soils have been discussed by Davies (1933) and he suggested N/500 HCl as a suitable dispersing agent.

The following observations were made in the course of the present investigation with respect to the andesitic ash soils.

1. The Whenuapai soil, which contains at the most only a trace of gibbsite, dispersed satisfactorily in dilute ammonia solution, the pH of the suspension being 10·4. The soil was first treated with hydrogen peroxide as in the International method of mechanical analysis, but the treatment with N/5 acid was omitted. The clay content found was 64·6

per cent. The same figure was obtained when analysed by the hydrometer method of Bouyoucos using sodium oxalate and sodium silicate as dispersing agents. N/500 HCl was much less effective as dispersing agent, the clay content found being only 34·6 per cent.

2. The stable ammonia dispersion of the Whenuapai soil had added to it a suspension made from undried soil equivalent to about 10 g. dry weight of the Ngapenga Road soil containing, as estimated from the thermal analysis curve, about 10–20 per cent. gibbsite. After daily shaking for 1 week, very definite flocculation had occurred. Examination of the filtrate showed, however, a negligible amount of alumina in solution.

3. A dispersion of the clay fraction of the soil from the Mairoa ash shower in N/200 HCl (pH of dispersion = 4·1) was strongly flocculated by the addition of N/10 ammonium hydroxide when the pH reached 6·6, signs of flocculation beginning at pH = 5·9. Further addition of ammonia to bring the pH to 11·4 did not produce dispersion. On boiling with N/10 NaOH, centrifuging off, and shaking with water, dispersion was obtained. Addition of N/5 HCl to this NaOH dispersion produced flocculation at pH 9·6, but redispersion did not occur at any stage on adding acid sufficient to give a final pH of 2·5. On centrifuging off and shaking with N/200 HCl, dispersion was again obtained.

A probable explanation of the observations made by Davies and those described above is that we are dealing with two colloidal systems of different iso-electric points capable of mutual coagulation under the appropriate pH conditions, these being allophane on the one hand and aluminium or ferric hydroxide on the other. The third experiment above suggested that the iso-electric point of allophane is slightly on the acid side of neutrality, and this receives support from the work of Mattson (1930) on iso-electrically precipitated aluminium silicates. In fact he states that the iso-electric point of a floc with a composition $Al_2O_3(SiO_2)$ 1·09 is pH 6·6, which is the required hydrogen-ion concentration for strong flocculation found in experiment 3. It appears to be accepted that the iso-electric points of $Al(OH)_3$ and $Fe(OH)_3$ are between pH 7 and pH 8. Consequently dispersion of a soil containing both allophane and free sesquioxides should be possible in a weakly acid medium (provided the anion concentration is sufficiently low) or in a strongly alkaline medium (provided the cation concentration is low enough). There seems to be also some critical concentration of iron or aluminium hydroxide in the soil, above which neither acid nor alkaline dispersing media are effective.

The observation of Davies that 'a soil which has been motor dispersed flocculates more rapidly and completely on the addition of any of the usual deflocculants than one that has not' has a likely explanation in that the sesquioxides which help cement the soil aggregates are set free thereby to exert their flocculating action.

There is no practical method in sight for completely dispersing soils containing all but traces of oxides of iron and aluminium as well as allophane. If the soil is known to be almost entirely free of sesquioxides, pretreatment with hydrogen peroxide, washing with water, and dispersion in a rotary shaker using an alkaline medium of pH about 10 appears to be

the most effective procedure. No acid pretreatment should be given with the intention of removing free sesquioxides as this is likely to cause partial decomposition of the allophane.

Summary

Allophane has been found to be the principal mineral in the clay fractions of soils derived from andesitic and rhyolitic volcanic ash showers in New Zealand. It is considered to be the common factor responsible for the characteristic physical properties of the andesitic ash soils. The chemical composition of the purest allophane separated from these soils varies similarly to that of geological specimens described by other workers. When deferration treatments are applied to the soil before separation of the clay fractions there can be considerable loss of alumina, although the characteristic differential thermal analysis curve of the mineral may still be obtained. If the deferration treatment is unduly prolonged the characteristic high temperature exothermic peak of allophane in the differential thermal curve may disappear.

The deferrated allophane clays take up appreciable amounts of alkali metals and could accordingly be considered to have high base-exchange capacity, although allophane has been considered previously to be in the low base-exchange capacity group of clay minerals. Allophane after ignition to 750° C. has a high capacity for adsorption of the dye Alizarin Red S, taking up about 70 per cent. of the quantity of dye adsorbed by gibbsite ignited under the same conditions. The difficulties found by previous workers in dispersing certain New Zealand volcanic ash soils are considered to be due to the association of allophane and free sesquioxides. Experiments by the writers lead to the conclusion that the isoelectric point of allophane is much closer to neutrality than is the case with the other clay minerals. Dispersion of soils containing allophane appears to be practicable only if the free sesquioxide content is low and the pH of the medium should at least be 10. Acid pretreatment should not be given owing to possible attack on the allophane, and a dilute acid medium does not appear to be a satisfactory solution to the problem of dispersing these soils.

Acknowledgements

The authors express their thanks to the following members of the Soil Bureau staff: Mr. J. P. Richardson for differential thermal analyses, Messrs. L. B. Robinson, R. F. Thomas, and M. Gradwell for preparation of clay and silt fractions of the soils examined.

REFERENCES

BERKELHAMER, L. H. 1944. An apparatus for differential thermal analysis. U.S. Bur. Mines Res. Investigation 3762.

Chem. Abstr. 1936, **30,** 993[4].

Chem. Abstr. 1948, **42,** 4877[e].

DAVIES, E. B. 1933. Studies in the dispersion and deflocculation of certain soils. N.Z. J. Sci. Tech. **14,** 228–32.

DION, H. G. 1944. Iron oxide removal from clays and its influence on base-exchange properties and X-ray diffraction patterns of the clays. Soil Sci. **58,** 411–24.

GRANGE, L. I. 1931. Volcanic ash showers. N.Z. J. Sci. Tech. **12,** 228–40.
HARDY, F., and RODRIGUES, G. 1939. Soil genesis from andesite in Grenada (B.W.I.). Soil Sci. **48,** 361–84.
Imp. Bur. Soil Sci. 1933. The dispersion of soils in mechanical analysis. Tech. Comm. No. 26, 31 pp.
JEFFRIES, C. D. 1946. A rapid method for the removal of free iron oxides in soils prior to petrographic analysis. Proc. Soil Sci. Soc. Amer. **11,** 211–12.
MATTSON, S. 1930. The laws of soil colloidal behaviour. III. Isoelectric precipitates. Soil Sci. **30,** 459–95.
—— 1931. The laws of soil colloidal behaviour. V. Ion adsorption and exchange. Soil Sci. **31,** 311–31.
PASK, J. A. and DAVIES, B. 1943. Thermal analysis of clay minerals and acid extraction of alumina from clays. U.S. Bur. Mines Res. Investigation 3737.
ROSS, C. S., and KERR, P. F. 1934. Halloysite and Allophane. U.S. Geol. Surv. Prof. Paper 185–G: 135–48.
TAYLOR, N. H. 1933. Soil processes in volcanic ash-beds. N.Z. J. Sci. Tech. **14,** 338–52.
WILLIAMS, C. H. 1950. Aust. J. Agr. Res. **1,** 156–64.

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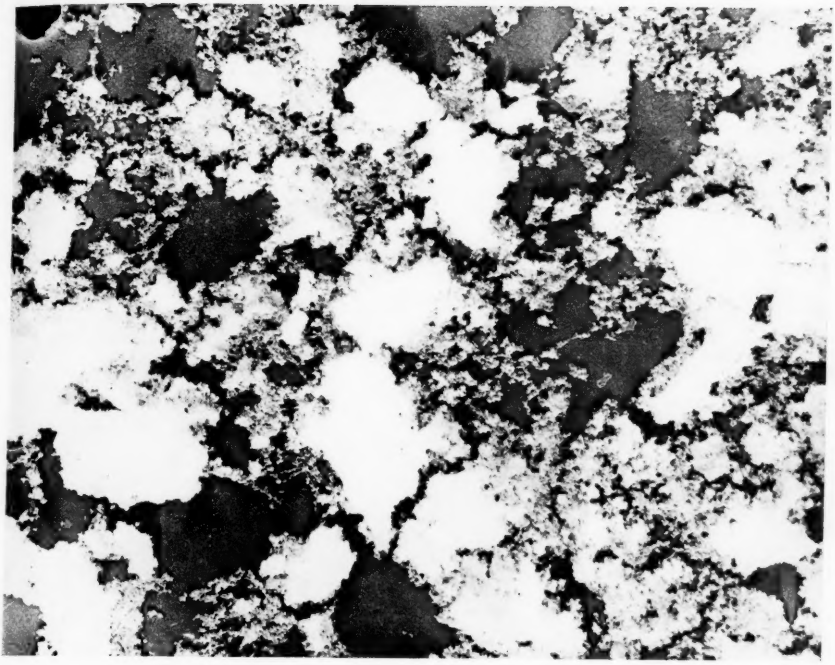

FIG. 2. Clay fraction 6c × 40,000

K. S. BIRRELL and M. FIELDES
PLATE I

THE DISTRIBUTION OF IRON AND ALUMINIUM OXIDES IN GLEY SOILS

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THE results of laboratory experiments on the process of gleying have been reported previously (Bloomfield, 1950, 1951). It has been shown in these experiments that ferric compounds are dissolved and that the iron content of the residual soil colloid may be reduced to a small fraction of the original value. Similar results have been reported by other workers (Halvorson and Starkey, 1927; Albrecht, 1941; Allison and Scarseth, 1942; Roberts, 1947; Bétrémieux, 1951).

In the light of this experimental evidence it is reasonable to assume that under natural conditions gleying would result in the more or less complete removal of iron from a gleyed horizon. This contention, however, is not supported by published analyses; in fact an accumulation of 'free' iron oxide in gley horizons is frequently indicated. Although not always described as such, it seems that in these cases the soil is of the 'mottled gley' type. In the case of mottled gley soils in the Yorkshire warplands it has been shown that the ferric oxide content is highest in what is apparently the zone of maximum gleying. As a possible explanation of this anomaly it has been suggested that the high values obtained for the ferric oxide are due to the presence of easily extractable ferrous compounds formed during the gleying (Heathcote, 1951).

Although the information contained in the literature is often not as complete as could be desired, it appears from the published analyses that if roots are unable to penetrate into the mineral soil, i.e. once true peat is formed, as is the case with a peat gley, mottling does not occur and iron is lost from the profile.

In this paper the results of an examination of two different types of gleyed soil from Lancashire are given. The first of these is an unmottled dark grey soil under 12 in. of peat from Rivington Moor (RM), and the second a pale grey soil showing extensive orange-brown mottling. The samples of the latter type (MCF) are from Moses Cocker Farm, where it was possible to select three sites within about 100 yards which showed varying degrees of impeded drainage and no apparent differences in the parent material.

Profile descriptions of the RM and one of the MCF soils are given below. Descriptions of all the MCF soils are not included since they differ only in the apparent degree of gleying, the drainage deteriorating from profile 1 to 3.

Profile RM

Locality: Rivington Moor. *Grid Ref.*: 3653/4158.
Elevation: 1,075 ft. *Relief*: Hilly.
Profile drainage: Very poor.

Parent rock: Glacial till of Carboniferous origin.
Vegetation: Molinia dominant, *Deschampsia flexuosa*.

12–0 in.	Molinia root mat overlying peat.
0–4 in.	Dark grey brown silty loam, fine cloddy structure; wet; pH 4.
4–9 in.	Dull brownish-grey sandy loam; tending to cloddy structure; wet; pH 4·3.
9–17 in.	Dull brownish-grey sandy clay loam; sub-angular sandstone fragments; wet; pH 6.
17 in.+	Greenish-blue grey sandy clay loam.

Profile MCF 2

Locality: Moses Cocker Farm, Rivington. *Grid Ref.*: 3639/4125.
Elevation: 780 ft. *Relief*: Footslopes in hilly country.
Profile drainage: Poor.
Parent Rock: Glacial till of Carboniferous origin.
Vegetation: *Nardus stricta*, *Deschampsia flexuosa*, *Juncus* sp.

2–0 in.	Peaty mat.
0–2 in.	Dull darkish grey peaty loam with fine rusty mottling; tendency to small prismatic structure; some iron oxide staining on root channels and structure faces; wet.
2–5 in.	Dark grey clay loam with much fine rusty mottling on structure faces and root channels; fine cloddy structure; moist.
5–9 in.	Dull grey clay with very little mottling on root channels; weak fine cloddy structure; some ferric oxide staining on pebbles and root channels; wet.
9–14 in.	Mainly pale grey clay with some fine orange spotting increasing downwards; moderate prismatic structure; wet.
14–24 in.	Orange and pale grey along root channels and structure faces in about equal amounts; clay; strong prismatic structure; wet.
24–36 in.	Brighter and more orange with pale grey on structure faces and root channels; slightly gritty clay; rather weaker prismatic structure; wet.
36 in.+	Dull olive-brown gritty sandy clay with much orange mottling; pale grey on root channels, weaker cloddy structure, very moist.

Experimental

Bulk analyses were carried out on all samples; in addition the grey and the brown stained materials from the MCF samples were separated by hand picking and examined separately. Depending on the amount of sample available, the total iron was determined either colorimetrically with $\alpha\alpha'$-dipyridyl or by titration with mercurous nitrate (Bradbury and Edwards, 1940; Kunin, 1942, 1943), after decomposition of the ignited sample with hydrofluoric acid and fusion of the residue with bisulphate. Free ferric and aluminium oxides were determined in acid ammonium oxalate extracts. After treatment with sulphuric acid the oxalate extracts were evaporated in silica dishes, ignited, fused with bisulphate, and dissolved in water. The aluminium was then determined colorimetrically by the aurine tricarboxylic acid, thioglycollic acid method (Chenery, 1948; Robertson, 1950) and the iron colorimetrically as before. Manganese and titanium were present in these soils in such small amounts that they were not considered.

The results are given in Tables 1 and 2.

TABLE 1

Rivington Moor

Depth (in.)	*0–4*	*4–9*	*9–12*	*12–17*	*17–21*	*21–27*
Total Fe_2O_3	0·5	0·8	0·8	1·6	2·4	3·0
Free Fe_2O_3	0·1	0·1	0·1	0·1	0·4	0·6
Free Al_2O_3	0·5	0·5	0·5	0·5	0·5	0·5

TABLE 2

Moses Cocker Farm

Profile	*1*			*2*			*3*				
Depth (in.)	*5–10*	*13–18*	*24–27*	*2–5*	*10–13*	*32–36*	*3–4*	*4–12*	*12–21*	*21–26*	*26–33*
Bulk samples:											
Total Fe_2O_3	4·3	6·2	6·3	3·7	4·4	5·5	3·6	3·7	3·4	4·8	5·7
Free Fe_2O_3	2·4	3·5	3·1	2·0	1·3	2·9	1·8	1·9	1·6	2·0	2·2
Free Al_2O_3	1·2	1·5	1·5	1·1	2·0	1·1	1·1	1·0	1·4	1·5	1·2
Brown separates:											
Total Fe_2O_3	..	..	8·0	..	11·7	8·6	..	16·9	9·5	10·7	11·9
Free Fe_2O_3	..	..	5·7	..	9·1	5·7	..	14·7	7·7	8·9	9·7
Free Al_2O_3	..	..	1·6	..	2·7	1·7	..	2·2	1·6	1·5	1·5
Grey separates:											
Total Fe_2O_3	..	..	3·6	..	2·6	2·3	..	2·1	2·8	3·1	3·4
Free Fe_2O_3	..	..	1·3	..	0·5	0·3	..	0·5	0·5	0·6	0·6
Free Al_2O_3	..	..	1·5	..	1·3	1·1	..	0·9	1·0	1·1	0·8

TABLE 3

Moses Cocker Farm: Difference between Total and Free Ferric Oxide

Profile	*1*	*2*		*3*			
Depth (in.)	*24–27*	*10–13*	*32–36*	*4–12*	*12–21*	*21–26*	*26–33*
Brown separates	2·3	2·6	2·9	2·2	1·8	1·8	2·2
Grey separates	2·3	2·1	2·0	1·6	2·3	2·5	2·8

Discussion

It is clear from Table 1 that a considerable amount of iron has been lost from the Rivington Moor soil. The figures indicate a solution effect which is gradually extending downwards. The figures for the mottled soils (Table 2), however, indicate a more complex system. In this case, while the analyses of the bulk samples show a fairly consistent decrease of the iron content with depth, a comparison of the figures for the grey and the brown separates shows that the iron content of the original soil varies very considerably over distances of only a few millimetres. During the separation of the grey and brown fractions it was seen that the iron-enriched material was usually located around root channels, suggesting that the variation of the iron content down the profile is mainly a function of the root distribution. (That iron enrichment occurs only around root channels does not appear to be universally true. In such soils as the

MCF it seems probable that at depth the ochreous patches represent as yet ungleyed rotten rock fragments rather than reprecipitated ferric oxide.) The appearance of a ferric oxide precipitate in the drainage water in the ditch at the bottom of the field shows that iron is indeed being lost from the MCF soil.

The MCF results also suggest that the formation of the ochreous mottling is not a part of the gleying process *per se*, but rather a secondary and opposing effect which is governed ultimately by the presence of root channels. For such mottled soils as this it seems that an estimate of the extent of the grey patches is the best measure of the intensity of gleying available at present, although it should be borne in mind that the time factor must also operate in determining the relative proportions of grey and brown material.

It can be seen that the total iron contents of the grey separates do not differ considerably. Table 3 shows that the difference between the total and free iron is reasonably constant, so that, in view of the difficulty of achieving a complete separation by hand picking, it seems highly probable that such differences as were found must be ascribed to brown material present as impurity. In other words, the iron content of the grey material appears to be constant despite the apparent differences in the intensity of gleying over the three sites. This constancy could be explained by the presence of iron-containing clay minerals (chlorite, &c.), but indications have been obtained which suggest that an additional factor is involved. While it was not found possible to extract any ferrous iron from the grey separates by means of buffered extractants, it was found that treatment with an alcoholic solution of $\alpha\alpha'$-dipyridyl caused the grey material to develop the characteristic pink colour of ferrous dipyridyl. It is thus clear that whatever the state of combination of the iron in the grey separates, it is not present in an easily extractable form, and that part, at least, is in the ferrous state. Work in progress at the time of writing indicates that the ferrous organic complexes formed by plant fermentation products (Bloomfield, 1951) may be sorbed on clay minerals. It is suggested that such an effect may be responsible for the ferrous content of the grey material and, possibly, for the grey colour of gleyed soils.

The constancy of the difference between the total and free iron applies equally well to the brown separates; following the above argument, this could mean that the whole soil has been gleyed and that the brown mottled patches have been formed by precipitation of ferric oxide on the grey substrate and not on original ungleyed soil.

The distribution of the aluminium in the two soils shows an interesting difference. Concentration of aluminium obviously takes place in the MCF soil, the distribution following that of the iron. In the RM soil, however, the aluminium content does not change significantly down the profile. This latter fact suggests that whatever the form of the aluminium which was extracted in the oxalate treatment, it is not present in the soil in a particularly readily soluble form, since otherwise it would be expected that the aluminium would have been removed from the upper layers in the same manner as the iron, and would in consequence have a similar distribution down the profile.

Summary

1. The iron content of mottled gley soils is essentially that of the ochreous mottles, the formation of which, it is suggested, is a secondary effect of the process of gley formation.

2. In a peat gley or in the grey fraction of a mottled gley soil, where secondary reprecipitation of the iron does not obscure the initial processes, gleying causes extensive mobilization of iron.

3. In the mottled gley soil considered here, the distribution of the readily extractable aluminium is the same as that of the free ferric oxide. It is apparent that the concentration of aluminium is governed fundamentally by the causes responsible for the formation of the ochreous mottles, since in the peat gley soil where the solution of iron is, if anything, more intense, the extractable aluminium remains constant down the profile despite the presence of as yet unattacked ferric oxide in the lower levels.

4. It is tentatively suggested that gleyed soil, i.e. the grey material, consists, at least in part, of a sorption complex between ferrous organic compounds and the clay mineral.

Acknowledgements

The author wishes to express his indebtedness to Dr. I. Stephen for making the mineralogical examination of heavy minerals, to Dr. A. Muir for helpful criticism and advice, and to Mr. E. Crompton for the profile descriptions, for assistance in the selection of suitable sites, and for much valuable discussion.

REFERENCES

ALBRECHT, W. A. 1941. Calcium saturation and anaerobic bacteria as possible factors in Gleization. Soil Sci. **51**, 213.

ALLISON, L. E., and SCARSETH, G. D. 1942. A biological reduction method for removing free iron oxides from soils and colloidal clays. J. Amer. Soc. Agron. **34**, 616.

BÉTRÉMIEUX, R. 1951. Étude expérimentale de l'évolution du fer et du manganèse dans les sols. Annales Agron. 193.

BLOOMFIELD, C. 1950. Some observations on gleying. J. Soil Sci. **1**, 205.

—— 1951. Experiments on the mechanism of gleying. Ibid. **2**, 196.

BRADBURY, F. R., and EDWARDS, E. G. 1940. A new method for the volumetric determination of ferric iron. J. Soc. Chem. Indust. **59**, 96.

CHENERY, E. M. 1948. Thioglycollic acid as an inhibitor for iron in the colorimetric determination of aluminium by means of 'Aluminon'. The Analyst, **73**, 501.

HALVORSON, H. O., and STARKEY, R. L. 1927. Concerning the importance of microorganisms in the solution and precipitation of iron. Soil Sci. **24**, 381.

HEATHCOTE, W. R. 1951. A soil survey on warpland in Yorkshire. J. Soil Sci. **2**, 144.

KUNIN, R. 1942. Determination of iron in soils and silicates by the mercurous nitrate method. Soil Sci. **53**, 211.

—— 1943. Micro-determination of iron by the mercurous nitrate method. Ibid. **55**, 457.

ROBERTS, J. L. 1947. Reduction of ferric hydroxide by strains of *Bacillus Polymyxa*. Ibid. **63**, 135.

ROBERTSON, G. 1950. The colorimetric determination of aluminium in silicate minerals. J. Sci. Food and Agric. **2**, 59.

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RENDZINA SOILS OF COASTAL FLATS OF THE SEYCHELLES

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WITH TWO PLATES

THE islands and islets of the Seychelles Archipelago are of two very different geological formations: granite and coral. The granite islands are twenty-eight in number and consist of three groups which lie on the 40-fathom line of the extensive Seychelles bank in the Indian Ocean between latitude 4° and 5° S. and longitude 55° and 56° E. These groups are Mahé and its satellites, Praslin and its satellites, and Silhouette with its neighbour North Island. Frigate, situated 30 miles east of Mahé, is isolated from these three groups.

The islands of the three groups are steep and rugged mountainous masses, the larger islands being higher and steeper than the smaller islands. The various peaks occur in ridges running along the longer axes of the islands, with numerous lateral spurs. Mahé, the largest island, is 32,500 acres in area and rises up to 2,993 ft. at Morne Seychellois. The next island in size, Praslin, is 9,700 acres in area, but its highest peak is only 1,281 ft. high. Silhouette, which is the third largest island, is 4,900 acres in area and its highest peak, Morne Dauban, is 2,600 ft. high. The rest of the larger granitic islands, La Digue, Curieuse, and Félicité, are 2,500, 900, and 689 acres in area and have peaks of 1,071, 587, and 747 ft. respectively. The total area of the granitic islands is about 55,000 acres.

As a result of their topography, the Seychelles granitic islands have not much land of agricultural value. In fact, apart from a restricted area under certain foot-hills and middle-slopes, which can be cultivated if terraced, the only agricultural land available in these islands consists of calcareous and sandy coastal flats, or 'plateaux'. These, although restricted in area, totalling some 3,150 acres, bear a large part of the main crop of the archipelago. The annual production of copra from the 'plateau' coconut groves is estimated at 1,000 tons, while the total production of the colony is about 6,000 tons per annum.

The climate of the granitic islands of the Seychelles is tropical, with little temperature variation throughout the year, a high relative humidity, and a very irregularly distributed rainfall. The mean daily temperature is about 82° F., with a range of about 5 to 7°. Relative humidity varies between 70 and 80 per cent. Rainfall varies from year to year, from island to island, and according to altitude: the sea-level average at Mahé is 97 in. per annum and at Praslin it is 70 in. Rainfall at higher altitudes may be roughly twice that at sea-level. The islands lie just at the northern limit of the south-east trade winds, which blow for about 6 months, from the end of April to the beginning of October. This is the driest part of the year. The north-west monsoon prevails during the rest of the time. This monsoon is the north-east monsoon of the India seas which, south of the equator, swings round from north-easterly to north-westerly. The

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north-west monsoon is characterized by a slightly higher temperature and by heavy showers. There are periods of calm and the strength and direction of the wind vary to a considerable extent. December and January are usually the wettest months. March is the hottest month and August is the coolest.

Distribution and Origin of the Plateaux

As already explained, 'plateaux' are long flat narrow coastal strips of coral and shell debris occurring along the creeks and bays of the granitic islands. Although they may be several miles long they are rarely more than half a mile wide. Inland they are limited either by foot-hills or mountain sides, or by the calcareous marshes frequently found at the base of foot-hills. Plate I shows the appearance of a 'plateau' viewed from the hill-side.

The parent materials of the 'plateaux' have obviously been the coral reefs of the granitic islands and the shells of the marine organisms of the shallow coastal lagoons. The formative agents have been the sea and the wind. The sea is responsible for the disintegration of the corals and shells and for heaping the disintegrated materials along the coast of the islands. To the wind, on the other hand, may be attributed the spreading of the heaped materials into the creeks and bays. Another important agent in the case of such highly calcareous soils as the 'plateau' soils must be vegetation, owing to the disintegrating action of roots and the dissolving action of decomposing organic matter. This seems to be substantiated by the fact that those 'plateau' soils with a higher content of organic matter are those with a higher proportion of fine sand (see Table 1).

Vegetation of the Plateaux

The 'plateaux' bear no natural vegetation. They are almost entirely covered by coconut (*Cocos nucifera*), but there are in addition small patches under vanilla (*Vanilla planifolia*) or 'cèdre' (*Casuarina equisetifolia*). Other cultivated plants are *Dioscorea alata*, *Ipomoea batatas*, *Lycopersicum galeni*, *Nicotianum tabacum*, *Zea mais*.

Among common trees and shrubs of the 'plateaux' are the following: *Calohyllum inophyllum*, *Cinnamomum zeylanicum*, *Hernadia peltata*, *Hibiscus tiliaceus*, *Pleomele angustifolia*, *Scaevola frutescens*, *Tecoma Leucoxylon*, *Terminalia catappa*, *Rhespesia populnea*, *Tournfortia argentea*.

There is also an undergrowth of annual and perennial creepers and herbaceous plants. They include the following: *Acalypha sanderiana*, *Asystasia corromandeliana*, *Cassia occidentalis*, *Crotalaria anagyroides*, *Cynodon dactylon*, *Euphorbia pilulifera*, *Ipomoea glaberrima*, *Isotoma longiflora*, *Lochnera rosea*, *Mimosa pudica*, *Polanisia viscosa*, *Portulaca oleracea*, *Stachytarpheta indica*, *Stenotaphrum conplanatum*, *Striga hirsutum*, *Turnera ulmifolia*, *Verbena bonariensis*.

Among the cultivated plants of the 'plateaux' none does better than the coconut palm. This is so true that the Seychellois planter pays little

attention to his 'plateau' coconut groves beyond giving them a periodical cleaning, which consists in the removal of cinnamon and other shrubs invading from the hill-sides. The successes of the coconut in the conditions of the 'plateau' may partly be attributed to two factors: first to the very open texture of the soils, and second, to their situation at the base of foot-hills or mountains, whose drainage water, enriched with dissolved nutrients, is available to the coconut roots.

Composition of the Soils

A typical 'plateau' soil profile is made up of two horizons: an A horizon, grey to black in colour, 1 to 12 in. in depth, consisting of single-grained

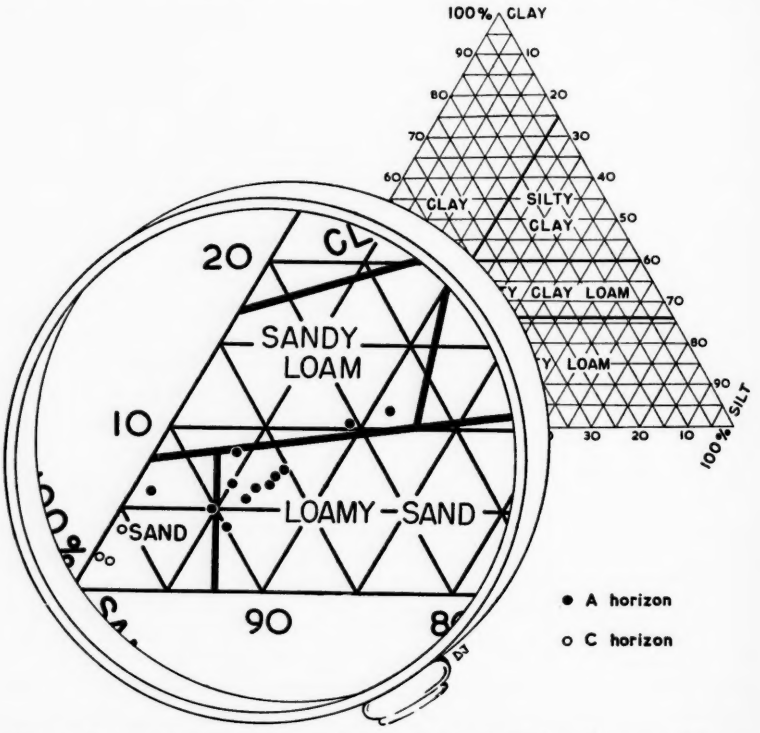

FIG. 1. Composition of soils plotted on T. J. Marshall's (1947) texture diagram.

sands or loamy sands and containing all the small coconut roots, and a C horizon, made up of white single-grained calcareous sand, 3 to 5 ft. in depth, extending down to water-table and containing the large coconut roots. In some instances two sub-horizons may be differentiated in the A horizon: a top layer, black in colour and from 1 to 3 in. deep, and a lower layer, lighter in colour and from 8 to 10 in. deep. Sometimes an AC horizon also occurs; it is 5 to 6 in. deep and light grey in colour.

However, in the majority of cases the line of division between the A horizon, containing organic matter, and the shining white C horizon is very distinct, although wavy in outline at some places. It frequently happens that a hard impervious calcareous pan, known locally as 'platin', is found just above or at a small distance above the water-table. This hard pan, a fine-grained conglomerate of calcium carbonate deposited from

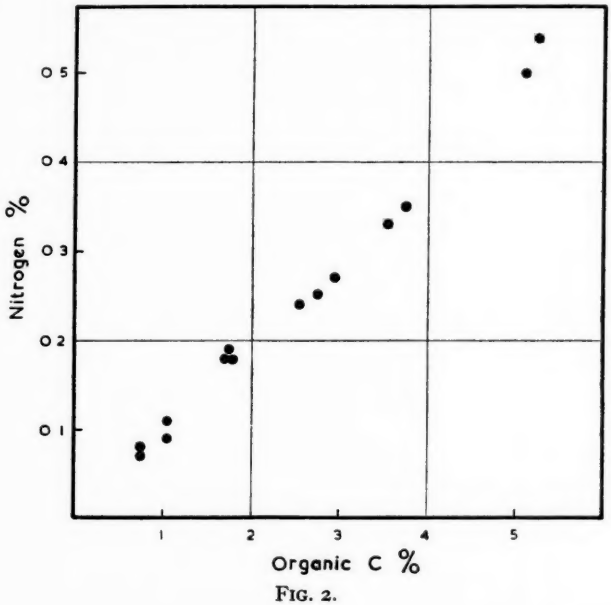

FIG. 2.

rain-dissolved calcium bicarbonate, is impenetrable to deep coconut roots going down to the water-table and is often an obstacle to successful coconut plantations. Plate II shows a typical 'plateau' soil profile. The classification of a number of 'plateau' soils is shown in Fig. 1. This is part of a triangular texture diagram as devised by T. J. Marshall on the basis of experience in Australia. Details of the mechanical analyses are given in Table 1.

From the standpoint of chemical composition the most important feature of the 'plateau' soils is, of course, their high content of calcium carbonate. The amount of carbonate, expressed as calcium carbonate, of the various samples examined was found to vary from 80 to 90 per cent.

As would be expected, the pH of the 'plateau' soils is high, being about 8·0, showing thus a definite though slight alkalinity.

As already pointed out, the A horizon of the 'plateau' profile contains all the organic matter; the C horizon usually contains little or none. The content of the A horizon itself varies to a considerable extent: figures as low as 1 per cent. and as high as 9 per cent. of organic matter were

TABLE I

Composition of Sands, Loamy Sands, and Sandy Loams from the Seychelles

Constituents are given as per cent. by weight on oven-dry soil

Soil no.	*Locality*	*Stones and gravels** %	*Coarse sand* %	*Fine sand* %	*Silt* %	*Clay* %	*pH*	*Air dry moisture* %	*Soluble salts* %	*Total carbonates* %	*Organic carbon* %	*Total nitrogen* %	*Carbon-nitrogen ratio*
7/48	Mahé	1	83	3	7	7	8·2	1·05	0·13	90	0·73	0·075	9·6
8/48 A	Curieuse	5	84	4	4	6	8·2	2·09	0·12	80	1·79	0·179	9·7
8/48 C	Curieuse	2	98	0	0	3	8·5	0·73	0·08	93	..	..	..
9/48	Mahé	1	83	7	6	5	8·2	1·30	0·11	81	1·06	0·115	9·1
4/49	Praslin	..	..	..	..	..	8·3	4·05	0·19	..	5·27	0·543	9·7
5/49	,,	..	..	..	..	..	8·1	3·03	0·14	..	3·77	0·350	10·7
6/49	,,	1	71	15	7	6	8·1	2·35	0·10	85	2·74	0·250	10·9
7/49 A	La Digue	1	88	5	1	6	8·0	1·29	0·09	82	0·73	0·077	9·5
7/49 C	La Digue	4	96	3	1	4	8·2	0·80	0·08	91	..	..	..
8/49	Praslin	3	45	40	7	7	8·1	3·00	0·10	81	2·95	0·272	10·8
9/49	,,	3	77	10	6	5	7·8	2·33	0·06	89	2·57	0·239	10·8
15/49	,,	0	43	36	9	9	8·0	2·26	0·15	80	1·71	0·180	9·5
18/49	Mahé	1	84	4	6	5	7·9	1·01	0·10	82	1·04	0·095	11·0
19/49	Praslin	2	82	8	5	5	8·3	1·79	0·16	80	1·73	0·191	9·0
20/49	La Digue	5	45	31	11	10	8·1	3·56	0·10	81	3·54	0·334	10·6
22/49 A	Mahé	10	77	8	2	6	7·9	4·54	0·17	80	5·08	0·501	10·1
22/49 C	Mahé	1	90	8	1	2	8·2	0·63	0·08	91	..	..	..

* Including plant roots.

obtained in the course of laboratory examinations. The average is between 2 and 3 per cent. As is shown below, the organic matter of the 'plateau' soils has a very important bearing on their moisture content and cation-exchange capacity.

The total nitrogen content of the A horizon is generally fairly high and in some cases good. Samples containing as much as 0·5 per cent. total nitrogen were found.

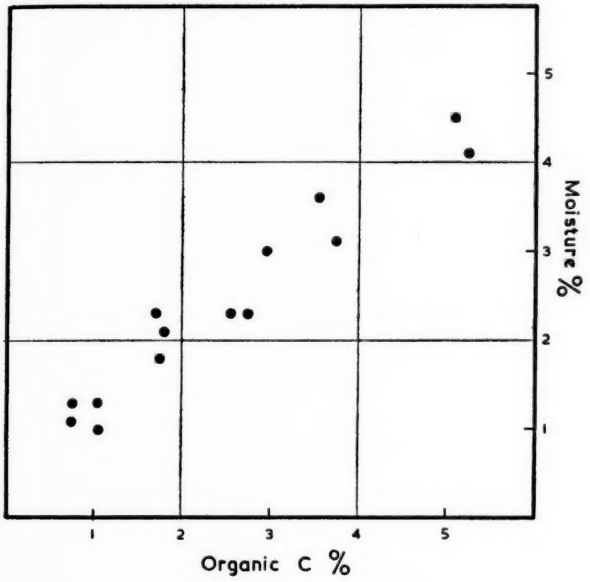

FIG. 3.

The carbon-nitrogen ratio of the A horizon is on the whole quite satisfactory, being about 10·0. Fig. 2 shows the nearly rectilinear relationship between the total nitrogen content and the content of organic carbon in a number of A-horizon samples.

The air-dry moisture content of the A horizon is generally low. This might be expected from the very light texture of the 'plateau' soils. With high content of organic matter, however, the moisture content is fair. Samples containing 9 per cent. organic matter were found to contain as much as 4 per cent. air-dry moisture. On the other hand, samples containing 1·25 per cent. organic matter were found to contain only 1 per cent. air-dry moisture. This shows the extent to which the moisture-holding capacity of the 'plateau' soils depends on their content of organic matter. As illustrated in Fig. 3, there is a nearly rectilinear relationship between the content of organic carbon and air-dry moisture content.

The analysis of strong-hydrochloric-acid extracts of A-horizon samples of 'plateau' soils gives an indication of their mineral composition, as can

be seen from Table 2. The percentage of calcium is very high and magnesium is present in considerable amounts. Potassium contents are low,

TABLE 2

Constituents soluble in Strong Hydrochloric Acid

Soil no.	CaO %	MgO %	K_2O %	P_2O_5 %	Fe_2O_3 %	MnO %	*Exch. capacity* m.eq./100g.
7/48	42·68	1·909	0·19	0·146	0·086	0·005	1·155
8/48A	45·78	1·891	0·017	0·498	0·034	0·004	2·094
9/48	44·17	2·045	0·026	0·220	0·115	0·008	1·310
4/49	40·65	4·508	0·027	0·626	0·071	0·002	..
5/49	49·50	1·569	0·012	0·460	0·084	0·003	..
6/49	49·87	1·246	0·026	0·353	0·044	0·004	2·940
7/49A	52·01	1·811	0·029	0·157	0·012	0·003	1·098
8/49	47·00	2·059	0·032	0·481	0·039	0·004	3·001
9/49	50·78	1·867	0·012	0·317	0·011	0·005	2·690
15/49	46·00	1·835	0·015	0·247	0·036	0·006	1·724
18/49	48·88	1·640	0·014	0·244	0·013	0·003	1·322
19/49	40·97	3·281	0·021	0·322	0·100	0·008	2·021
20/49	45·75	1·935	0·036	0·552	0·053	0·005	3·339
22/49A	45·78	2·367	0·061	0·500	0·094	0·002	4·943

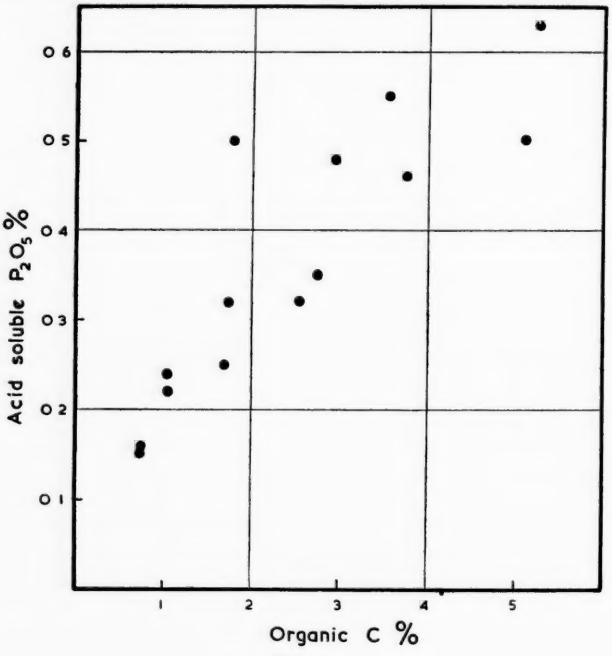

FIG. 4.

but the element is presumably present in sufficient quantities for normal plant growth. Acid-soluble phosphorus varies considerably and tends to

be present in large amounts where the content of organic matter is high. The fairly well marked linear relationship between organic carbon and acid-soluble phosphorus is illustrated in Fig. 4. This suggests that the greater part of the phosphorus of the 'plateau' soils exists in organic form. Iron and manganese are found in extremely low concentrations. In the presence of a large quantity of calcium, with its well-known inhibitory action, this should result in iron and manganese deficiencies.

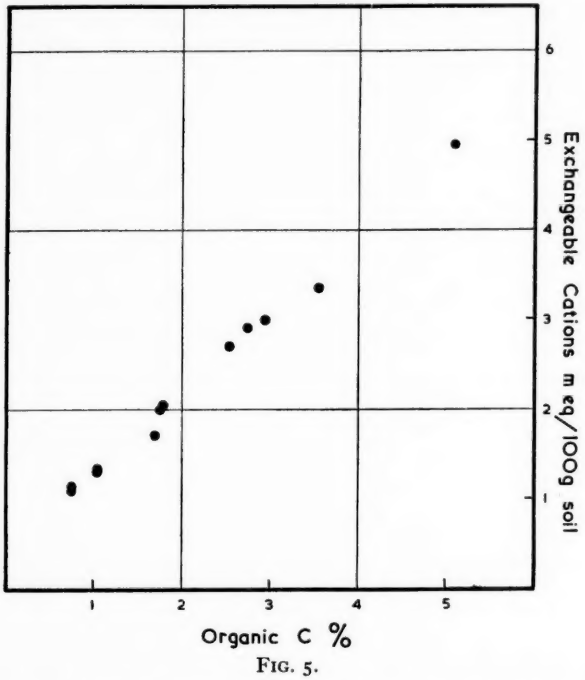

FIG. 5.

This seems to be actually the case, as is shown by the common occurrence of intervenal leaf chlorosis of a certain number of plants, of perosis in chickens, and of anaemic symptoms noted among cattle of the 'plateau'.

The total exchange capacities of A-horizon samples are also shown in Table 2. As illustrated in Fig. 5, there is a marked linear relationship between the content of organic carbon and of exchange capacity in the A horizon. This suggests that the process of cation exchange is almost solely due to colloidal organic matter.

Methods of Examination

The samples of 'plateau' soils examined in the course of the present study were collected from the more important islands of the archipelago. In all fifteen A-horizon samples and three C-horizon samples were collected. Cursory field examinations easily revealed the rather regular

coarse-sand texture of the C horizons, so that it was thought unnecessary to sample and examine different layers of the C horizons.

The thoroughly mixed samples were all air-dried before examination.

The C-horizon samples were examined for texture, soluble salts, pH, air-dry moisture, and total carbonates.

The A-horizon samples were first examined for texture, pH, soluble salts, air-dry moisture, total carbonates, organic carbon, and total nitrogen. Secondly, they were examined for their acid-soluble constituents by extraction with strong hydrochloric acid. The acid-soluble constituents that were determined were the four major mineral elements calcium, magnesium, phosphorus, potassium, together with iron and manganese, the determination of which was considered important on account of their low concentration. Thirdly, the samples were examined for their exchange capacity.

The following is a short description of the analytical methods employed:

Stones and gravels. Prior to mechanical analysis the samples were passed through a 2-mm. sieve, all the retained particles being recorded as stones and gravels. It must be mentioned here that a large part of the stones and gravels of the 'plateau' samples consists actually of root fragments, which accounts for certain high figures of samples containing numerous roots.

Texture. Mechanical analysis of 'fine-earth' fractions was carried out using the pipette method. The particle-size groups adopted were those of the International System. Destruction of organic matter was performed with hydrogen peroxide.

pH was determined in a Lovibond comparator.

Soluble salts were determined from water extracts of the samples, after filtering through a filter-candle. The soluble salts of the samples examined consisted mainly of chlorides.

Air-dry moisture was determined in an oven at 105° C.

Total carbonates were determined by the rapid titration method (Piper, 1947).

Organic carbon was determined by Walkley and Black's rapid titration method (Piper). The factor 1·724 may be used to convert these figures to organic matter. *Total nitrogen* was determined by Kjeldahl's method.

Strong-hydrochloric-acid extracts were obtained by using the Agricultural Education Association's method.

Acid-soluble calcium was precipitated as calcium oxalate and was determined by titration with potassium permanganate. *Acid-soluble magnesium* was weighed as magnesium pyrophosphate after precipitation as magnesium ammonium phosphate. *Acid-soluble potassium* was determined as the perchlorate. *Acid-soluble phosphorus* was precipitated as ammonium phospho-molybdate and was determined by solution in standard sodium hydroxide and back-titration with standard acid. *Acid-soluble iron* was determined colorimetrically in a Lovibond tintometer with ammonium thiocynate. *Acid-soluble manganese* was also determined colorimetrically in a tintometer with sodium bismuthate.

Exchange capacity was determined by leaching with ammonium acetate

I. 'Plateau' landscape, viewed from hillside

II. A typical 'plateau' soil profile

J. F. G. LIONNET—PLATE I

solution at pH 9·0, distilling the absorbed ammonia into standard acid, and back-titrating with standard alkali.

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REFERENCES

MARSHALL, T. J. 1947. Mechanical composition of soil in relation to field description of texture. Austr. Counc. Sci. Indust. Res. Bull. 224.

PIPER, C. S. 1947. Soil and plant analysis. Melbourne University Press.

A COMPARATIVE STUDY OF SOME SOIL NUTRIENTS IN THE CORALLINE SUGAR-CANE SOILS OF BARBADOS

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In a paper describing the chemical relationships between the seven recognizable coral-limestone soil groups of Barbados published by Saint (1934) was included a series of mean analytical figures for each of these soil groups. These results not only served as generally representative indices for the coralline soil groups, but certain of them were also applied in relation to advisory work on the manuring of sugar-cane. Further and more important with respect to the work undertaken and reported in this paper, the soil samples analysed were comprised of separate field samples for each soil group of which full record has been kept. This first sampling took place between the years 1929 and 1932.

In 1947 the same technique of field-to-field sampling over these soils was carried out. Where possible, and this was in the majority of cases, the same fields were sampled. Some of the original fields, however, were under a cane crop, in which case adjacent fields were sampled. Where fields had been joined together, the whole rearranged area was sampled. The samples so taken have been analysed by similar methods to those employed by Saint in his original work (1934).

It is now possible to compare the two sets of data obtained in the light of agricultural advancement (particularly change of manurial policy) during the period of time between the sampling, an interval of 15 to 18 years.

Description of Coralline Soils

Saint (1934) identified seven different soil groups by means of colour and elevation above sea-level, and showed that they were chemically related. All, with the exception of one minor group, are clay soils containing between 50 and 70 per cent. clay, have topsoil pH's above 7, and vary in colour from black at lower elevations through intermediate chocolate-brown and brown to red at higher elevations. In the case of the red soils this high pH in the surface soil is attributed to heavy marling in the past.

The red soils have been termed generally Terra Rossa type and the black soils Rendzina type. Hardy (1950) refers to them as Terra Rossa (Red Podzolic; Pedalfer; zonal) and Rendzina (Calcimorphic; intrazonal).

Factors affecting Soil Fertility

During the period between sampling, i.e. 1929–32 to 1947, there has been a steady mean increase in sugar-cane yield per acre in Barbados (Foster, 1936–50; Stevenson, 1951). This is attributed to the effects of new sugar-cane varieties from the B.W.I. Sugar-Cane Breeding Station,

longer ratooning of canes, improved cultivation with mechanical equipment in recent times, and the change of manurial methods that has taken place since 1928.

Of these factors manuring has undoubtedly been the greatest contributor to relative yield increase as well as the maintenance and building up of soil fertility. Before presenting the results obtained it is desirable to consider the manurial picture for sugar-cane on these soils before and after the first sampling period (1929–32).

Prior to 1928, it was general estate practice to give plant canes a minimum of 8 tons—often 30–60 tons—per acre of pen manure with the addition of some artificials (nitrogen and potash). The artificials were applied in two dressings, an early manure in January to the young plants (2 months old) and a late manure with the rains in July. Ratoons were given 1 cwt. per acre of nitrate of potash only after cutting. If sufficient pen manure was not available—and stock were often kept for the sole purpose of making pen manure—it was thought necessary to apply organic nitrogen in the form of sheep, fish, or cotton-seed meal manures.

Trials carried out by Saint (1932) between 1928 and 1932 confirmed the opinion that the principal factors affecting the yield of sugar-cane in Barbados are water, potash, and nitrogen; phosphates are ineffective.

The most important findings of these preliminary trials by Saint were that artificials plus mulch gave equally good yields of cane as pen manure, and at much less cost. Moreover, on potash- and/or nitrogen-deficient soils, the maximum yield of cane could not be obtained by the use of pen manure only. Applications in excess of 10 to 15 tons per acre had little further effect on the yield of cane, and little or no residual value.

It was found also that the conservation of soil moisture during the dry season (December to May) obtained by the use of sour grass (*Andropogon Pertusus*) or trash mulches resulted in an increase of from 4 to 6 tons of cane per acre. It was recommended that the humus content and therefore the drought resistance of the soil should be maintained and increased by the use of these mulches. Thus the manuring of sour-grass pastures to produce a greater bulk of mulching material was undertaken by estates, with a resulting increase of organic matter applied to these soils.

Nitrogen and potash are considered together since it was found in the very early stages of the manurial work that maximum yield of cane per acre depended to some extent on the interaction between these two plant nutrients as well as to each one individually. Quantitatively, 60–80 lb. of available nitrogen and 80–100 lb. of available potash were sufficient to grow the maximum crop of both plant canes and ratoons on these coralline soils under the traditional hand-tillage system of cultivation, i.e. cane holes (Saint, 1928–30).

Thus, since the publication of these results, and in the light of recent trials which have confirmed this work (Robinson, 1949, 1951), the manurial recommendations of the Department of Science and Agriculture based on these findings have been in general practice.

The analytical results of the first soil sampling (Series A: 1929–32)

are considered here to be indicative of the fertility status of the coralline soils under the older system of manuring, and the analytical results of the second soil sampling (series B: 1947) are considered to be indicative of the change in soil-fertility status under the present system of manuring.

Analytical Results and Discussion

i. *Organic carbon*

Reference to Table I will show the relationship between results obtained for five coral-limestone soil groups by Saint in 1934 (Series A) and those obtained on the more recent soil samples in 1947 (Series B). (The designation Series A and Series B will be used as a reference for the two sets of results throughout.)

TABLE I

Organic Carbon Content of Coral Limestone Soils (per cent. Organic C)

Soil group	*No. of determinations*		*Mean*		*SE. of Mean*	
	A	*B*	*A*	*B*	*A*	*B*
Red (over 700 ft.) . .	10	18	1·57	1·94*	±0·090	±0·082
Intermediate Red (400–700 ft.)	5	4	1·48	2·20*	±0·064	±0·193
Intermediate Black (200–400 ft.)	8	10	1·35	1·90*	±0·071	±0·136
Christ Church Ridge (200–400 ft.	15	14	0·96	1·54	±0·056	±0·333
Black (0–200 ft.) . . .	18	11	1·16	1·65†	±0·058	±0·196

* Significant at $p = 0{\cdot}01$. † Significant at $p = 0{\cdot}05$.

Note: The organic carbon determination was made using a modification of Hardy's (1928) wet combustion method.

The results for the 1947 samples indicate a higher soil organic-carbon content which very closely parallels the 1934 results for the same soil groups. This is attributed primarily to the manuring of sour grass giving increased yields of organic matter for mulching; to sugar-cane variety improvement leading to longer ratooning of the crop and, in the case of several of the leading varieties such as B. 37161, to heavier trashing of the cane. (Unlike many sugar-cane areas, cane trash is not burnt prior to reaping the crop in Barbados.) The practice of mulching has resulted in all first-crop cane fields receiving a considerable dressing of organic matter applied in such a manner that decomposition and breakdown products become available in the soil as a regular, continuous supply.

ii. *Total and exchangeable potash*

The indications from the rather limited number of samples examined are that there has been an increase in the total potash content of the black and red soil groups during the period between analyses (Table 2). Results for exchangeable potash on the seven soil groups (Table 3) show an increase though this is not statistically significant in every soil group.

TABLE 2

Total Potash Content of some Coral Limestone Soils (*per cent.* K_2O)

Soil group	*No. of determinations*		*Mean*		*Minimum*		*Maximum*	
	A	*B*	*A*	*B*	*A*	*B*	*A*	*B*
Red (over 700 ft.) .	12	12	0·1233	0·1652	0·0631	0·1030	0·1849	0·4715
Black (0–200 ft.) .	10	10	0·1328	0·1395	0·0947	0·1095	0·1951	0·1864

No significant difference between means.

TABLE 3

Exchangeable Potash Content of Coral Limestone Soils (*per cent.* K_2O)

Soil group	*No. of determinations*		*Mean*		*Minimum*		*Maximum*	
	A	*B*	*A*	*B*	*A*	*B*	*A*	*B*
Red (over 700 ft.) .	25	25	0·0161	0·0177	0·0042	0·0095	0·0391	0·0307
Inter. Red (400–700 ft.) . .	28	28	0·0123	0·0171*	0·0055	0·0101	0·0188	0·0446
Inter. Black (200–400 ft.) . .	10	10	0·0162	0·0194	0·0085	0·0121	0·0240	0·0367
St. George's Valley (100 ft.) . .	3	3	0·0139	0·0157	0·0117	0·0147	0·0167	0·0167
Red Sand (100–300 ft.)	7	7	0·0060	0·0118*	0·0031	0·0093	0·0096	0·0142
Christ Church Ridge (200–400 ft.) .	16	16	0·0145	0·0186†	0·0071	0·0120	0·0206	0·0302
Black (0–200 ft.) .	21	21	0·0252	0·0264	0·0080	0·0139	0·0540	0·0515

* Significant at $p = 0·01$. † Significant at $p = 0·05$.

Note: The methods of analysis used were (*a*) total potash-volumetric cobaltinitrite method after extraction of the soil with hydrochloric acid; (*b*) exchangeable potash-volumetric cobaltinitrite method after extraction with neutral ammonium acetate.

Although both the total and the exchangeable soil potash appear to have been increased by the general practice of applying 100 lb. of K_2O per acre per crop of cane, the number of samples analysed in the former case is so few as to preclude any general conclusion being arrived at. In the case of the latter, however, but in view of the fact that for some soil groups the increase is not statistically significant, it is only possible to

state that generally speaking there has been an increase in exchangeable soil potash on all the soil groups during the period between sampling. The increase is undoubtedly a result of longer ratooning with satisfactory quantitative potash application to each crop removed.

This conclusion is to be expected in the light of early soil-potash work carried out by Saint (1928–30) when he stressed this soil variation factor in any one soil group. Such a method of manuring as was adopted with potash would not influence greatly any original variation in field-to-field soil-potash content, a condition which will complicate the future detailed control of potash application.

iii. *Total and water-soluble phosphate*

Comparative analysis figures for total and water-soluble soil phosphate are given in Tables 4 and 5.

TABLE 4

Total Phosphate Content of some Coral Limestone Soils (per cent. P_2O_5)

Soil group	*No. of determinations*		*Mean*		*Maximum*		*Minimum*	
	A	*B*	*A*	*B*	*A*	*B*	*A*	*B*
Red (over 700 ft.) .	12	12	0·2065	0·1811	0·4112	0·3294	0·1377	0·0955
Black (0–200 ft.) .	9	9	0·2114	0·1919	0·5064	0·3004	0·0966	0·1039

No significant difference between means.

TABLE 5

Water-soluble Phosphate Content of Coral Limestone Soils (parts per million P_2O_5)

Soil group	*No. of determinations*		*Mean*		*SE. of mean*	
	A	*B*	*A*	*B*	*A*	*B*
Red (over 700 ft.) . .	27	26	0·14	0·15	±0·034	±0·046
Inter. Red (400–700 ft.) .	14	23	0·29	0·44	±0·038	±0·081
Inter. Black (200–400 ft.) .	12	13	0·61	0·33	±0·043	±0·133
Red Sand (100–300 ft.) .	6	8	0·20	0·20	±0·103	±0·030
Black (0–200 ft.) . . .	16	25	0·98	0·53	±0·173	±0·126

No significant difference between means.

Notes: The methods of analysis used were (*a*) total phosphate—volumetric ammonium-molybdate method after extraction of the soil with hydrochloric acid, (*b*) Water-soluble phosphate—colorimetric method of Atkins (1924) except that the colour developed was measured on a Hilger-Watts Spekker and compared with standard solutions.

In view of the lack of response to phosphatic fertilizer on these soils in all the manurial trials carried out since 1928 (Robinson, 1949), no deliberate fertilizer practice has been carried out. It is not, however,

correct to say that no phosphate has been returned to the land, since, in addition to occasional pen manure applications from the few stock left on the estates, it is customary to return the relatively small quantities of filter-press mud, and the boiler-house ash (from the bagasse used as fuel) obtained from the sugar factories to the land. No detailed rotational application is carried out, but over a series of crops grown in a natural rotation, such a method of application inevitably results in a crude form of rotational application to the fields. Often, however, fields close to the factory receive more frequent applications, while estates farther away from the factory get a lesser total quantity of these factory wastes than those close by. This has served to increase the magnitude of variation in the field to field phosphate content of any one soil group (Robinson, 1949*b*), and the results in Tables 4 and 5 are proofs of this variation.

Therefore no concise indication of soil-group phosphate relationship can be obtained from the analyses recorded in Tables 4 and 5. It can be said, however, that the results presented do not seem to show any very radical changes in soil phosphate for Series A compared to Series B in relation to soil group.

Summary

1. Samples of the coralline sugar-cane soils were taken on the several soil groups. Individual fields on different sugar estates in each soil group were first sampled between 1929 and 1932 (Series A), and the same fields were again sampled during 1947 (Series B). The samples of Series B were subjected to chemical analysis by the same analytical methods that were used for the first set of samples. A comparison of results was then made in terms of organic carbon, total and exchangeable potassium, total and water-soluble phosphate.

2. The time of first sampling corresponds very closely with the major changes in manurial policy on the sugar estates resulting from manurial trials carried out by Saint. Thus the analytical results of Series A can be said to correspond to the soil-nutrient conditions obtaining on sugar estates prior to these new manurial policies, and those of Series B to soil-nutrient conditions obtaining 15–18 years after the adoption of the new policies. During this 15–18-year period there have been no major changes in manurial practice on these soils.

3. A comparison of the results shows that during the 15–18-year period there has been a mean increase in soil organic carbon of 41 per cent. (significant at $p = 0{\cdot}01$) for the five major soil groups and a mean increase in exchangeable soil potash of 21·5 per cent. over all the soil groups recognized. Comparative results obtained for total soil potash are inconclusive; the total soil phosphate and water-soluble soil phosphate results are both variable and inconclusive.

(4) The author has placed the major emphasis on the manurial policy as affecting the comparison between analytical results obtained for soil samples of Series A and Series B. It is only correct to add that there are many factors influencing soil-nutrient properties, and that where possible these have been noted and/or discussed.

Acknowledgements

I wish to express my appreciation of the assistance and continued interest which has been accorded me by Sir John Saint, Kt., C.M.G., O.B.E., during the preparation of this paper, and to note that the original suggestion for this study was made by Sir John prior to his retirement as Director of Agriculture, Barbados. I should further like to record my thanks to Mr. L. A. Hall and Mr. E. W. Maxwell for their part in carrying out the numerous analyses.

REFERENCES

ATKINS, W. R. G. 1924. J. Agric. Sci. **14,** 192.
FOSTER, C. B. 1936–50. Yields of Sugar Cane in Barbados. (Annual Reports.)
HARDY, F. 1928. J. Agric. Sci. **18,** 740–65.
—— 1950. Report of Caribbean Commission Soils Conference, Puerto Rico, 1950, p. 17.
ROBINSON, J. B. D. 1949*a*. Barbados Dept. Sci. Agric. Bull. 14.
—— 1949*b*. Proc. B.W.I. Sugar Tech. Assoc. 48–62.
—— 1951. Unpublished data.
SAINT, S. J. 1929–30. Reports Barbados Dept. Sci. Agric.
—— 1932. Barbados Agric. J. **1,** No. 4, 1–23.
—— 1934. Ibid. **3,** 1–36.
STEVENSON, G. C. 1951. Private communication.

(*Received 10 September 1951*)

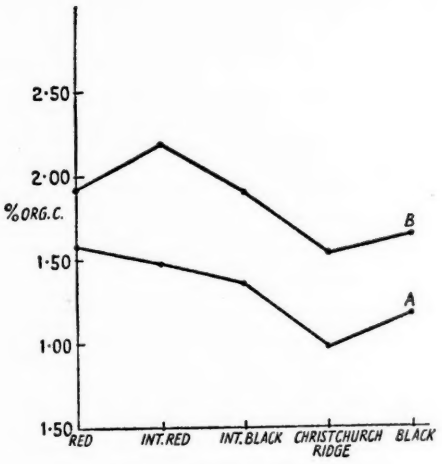

FIG. 1. Organic Carbon

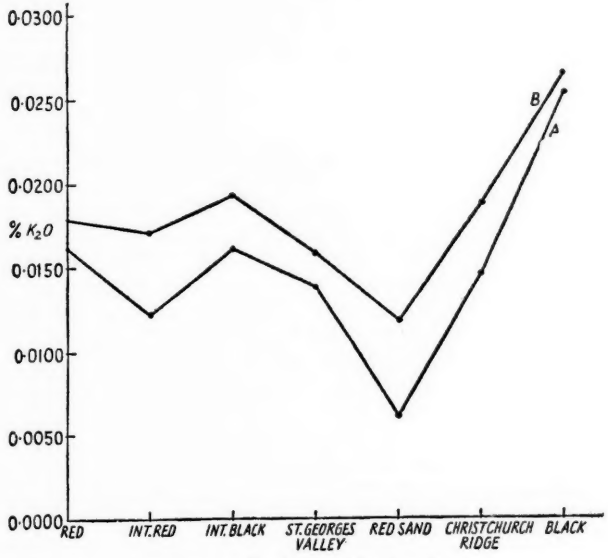

FIG. 2. Exchangeable Potash

STUDIES IN PEDOGENESIS IN NEW SOUTH WALES

III. THE ALPINE HUMUS SOILS

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WITH THREE PLATES

Introduction

THE alpine humus soils are most extensively developed in the Monaro region, which comprises the highest portion of the southern tablelands of New South Wales.

For the most part the Monaro lies between 2,000 and 3,000 ft. above sea-level. The western boundary, however, rises abruptly to the Snowy Mountains which include the most elevated country in Australia, the Kosciusko massif, where the maximum elevation of 7,328 ft. is attained on Mt. Kosciusko.

On ascending this western portion of the Monaro, four naturally defined tracts may be recognized: the tableland tract below 3,000 ft., the montane tract between 3,000 and 4,500–5,000 ft., the sub-alpine tract from the latter levels to the tree line at 6,000 ft., and the alpine tract above 6,000 ft.

Typical sub-alpine and alpine landscapes are shown in Plate I (*a*, *b*, *c*, *d*).

The present-day alpine and sub-alpine tracts of the Kosciusko area were the centre of the very limited glaciations experienced on the Australian mainland during the Pleistocene period. According to the most recent evidence (David, 1950), there were at least two series of glaciations at Kosciusko, the first series of ice-cap glaciations probably occurring in the Early Pleistocene and the second series of valley and cirque glaciations in the Late Pleistocene. Although the glaciations were responsible for the development of much characteristic glacial topography, they were not sufficiently extensive for the production of boulder clay, as they were in Europe and North America. Post-glacial pedogenesis in the Kosciusko area, therefore, has occurred mainly *in situ* either from the underlying country rock or to a less extent from morainic materials. As far as may be ascertained from their present environments, the soils studied in this paper have been formed under post-glacial conditions of physical and chemical weathering.

The alpine humus soils form the climatic climax soil of these alpine and sub-alpine environments. The profiles of this group show variations with altitude which can be reconciled with the theory advanced later for their genesis, but the feature which makes them of more than local interest is the considerable depth of profile, which at the altitudes of optimum development appears to be considerably greater than would be expected elsewhere in the world.

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Apart from a brief mention as skeletal high-moor soils (Prescott, 1931, 1944; Stephens, 1941, 1950) alpine humus soils have not been described previously in Australia. They are also known to occur in other

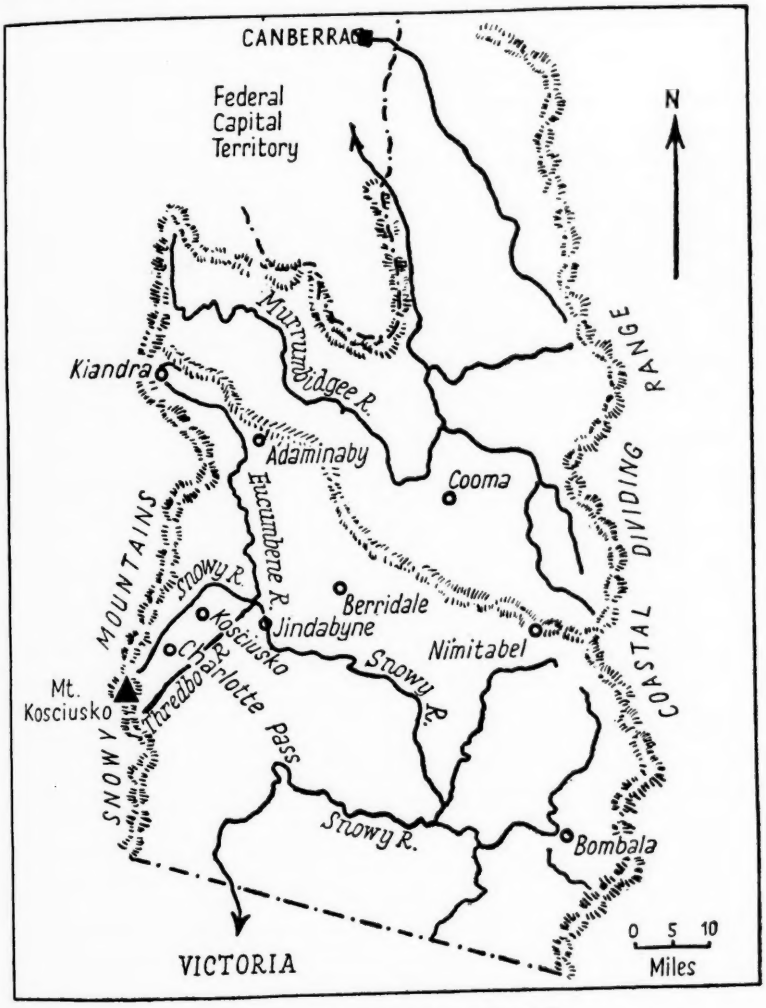

FIG. 1. The Monaro region of N.S.W.

alpine and sub-alpine environments in New South Wales, Victoria, Tasmania, and the Australian Capital Territory. The impression given by these other accounts is that they are skeletal, shallow, and immature (e.g. Stephens, 1941).

Alpine humus soils, also called alpine meadow, mountain meadow, and mountain soils, are characteristic of most alpine and sub-alpine regions of the world, but not apparently of the arctic and antarctic latitudes (e.g. Braun-Blanquet, 1932; Gibbs, Raeside *et al.*, 1945; Joffe, 1936; Robinson, 1949).

Environment

Climate

The most important features of the climatic environment are winter snow which persists on the ground continuously for at least 1 month, and a relatively warm summer. Average annual precipitations vary from 30 in. at lower sub-alpine levels up to 90 in. in the upper alpine tract. They are mostly of winter incidence and occur mainly as snow. Normal mean monthly temperatures range from a maximum of about 58° F. in midsummer to a minimum of 20° F. in midwinter. Severe frosts and wide daily temperature fluctuations are experienced. Except in windswept, snow-free situations, the alpine humus soils are protected from these very low winter temperatures by the overlying snow, which remains on the ground from 1 to 9 months, depending on altitude and aspect.

Physiography

Alpine humus soils develop under most conditions of slope, and in most situations except those which are extremely windswept or those where the water-table is at or near the surface.

Geology

The occurrence of these soils on a range from acid to basic rocks, including granite, gneiss, phyllite, slate, basalt, and limestone, emphasizes their position as the climatic climax. A factor of probable pedogenic importance is the addition of small quantities of wind-blown dust which is received most years from the arid regions of the interior.

Wind-blown calcareous dust has also been stated to be received on the European Alps, where its presence is said to favour the genesis of alpine humus soils instead of peaty and podzolized soils (Webb, 1947).

Vegetation

The alpine humus soils of the Monaro are associated with the following types of vegetation: sub-alpine woodland (5,000–6,000 ft.), heath (5,000–7,300 ft.), sod tussock grassland (5,000–7,300 ft.), tall alpine herbfield (above 6,000 ft.), and occasionally fjældmark (above 7,000 ft.).

The sub-alpine woodlands extend as the climatic climax over most of the better drained slopes of the sub-alpine tract. They are characterized by a continuous to discontinuous tree canopy of the snow gum (*Eucalyptus niphophila* Maiden and Blakely), well-developed shrub strata, and an extremely dense herbaceous sward dominated by the snow grass (*Poa caespitosa* Forst. f., *s. lat.*) (Plate I (*a*) and (*b*)).

Above the tree line, tall alpine herbfields replace the sub-alpine woodlands as the climatic climax of the alpine tract. These communities

consist of a dense sward of perennial alpine herbs, among which conspicuously flowering plants such as the snow daisy (*Celmisia longifolia* Cass.) are dominant or codominant with snow grass (Plate I (*c*) and (*d*)).

On more gently sloping, poorly aerated but not water-logged situations in the sub-alpine tracts, the climatic-climax woodland and herbfield vegetation is replaced by sod tussock grasslands. The latter communities consist of a dense sward of tussock-forming grasses dominated by *Danthonia nudiflora* P. F. Morris and a rigid form of snow grass (Plate I (*a*)).

Heath vegetation develops both on windswept situations and on the imperfectly aerated lesser slopes other than those affected by a water-table. The communities of the former situations usually consist of a continuous dominant stratum of shrubs up to 5 ft. high, of which *Oxylobium ellipticum* R. Br. and *Podocarpus alpinus* R. Br. are the most characteristic, underlain by a relatively sparse ground layer of snow grass. The heath communities of the gentler sloping situations, on the other hand, usually consist of a discontinuous dominant stratum of shrubs, typically species of *Epacris* and *Kunzea Muelleri* Benth., underlain by a semi-continuous layer of snow grass.

Fjældmark vegetation is restricted to the most exposed and windswept situations in the upper alpine tract. These communities are open, and dominated by dwarf, prostrate shrubs and herbs, of which *Epacris petrophila* Hook. f. and *Veronica densifolia* F. Muell. are the most characteristic.

The alpine humus soils described elsewhere in the literature typically occur above the tree line. On the Monaro, however, this restriction does not obtain, since they also are found under woodland vegetation. Indeed, they attain their optimum development under the sub-alpine woodlands described above. This may be attributable to the presence in the Monaro flora of tree species better adapted to severe conditions of cold, snow cover, and high wind velocities.

Soil Profile Descriptions and Analyses

Profile morphology

The profiles of the alpine humus soils are dominated by the organo-mineral horizons, and in the shallower profiles of the alpine tract these may penetrate into the decomposing rock (Plate III (*a*)). In the deeper profiles of the sub-alpine tract (Plate II (*a*) and (*b*)) the organo-mineral horizons are separated from the parent material by a diffuse zone of well-weathered mineral matter containing little humus. There are no sharp boundaries between the successive horizons, one gradually merging with the next. Floaters of undecomposed rock are present throughout the profile, ranging in size from small pebbles to large boulders, and there is also frequently a stone line, marking the average depth to which natural solifluction processes are active (Plate II (*b*)). The organo-mineral horizons show a friable crumb structure, but the subsoil horizons are more compact. The mountain earthworm *Megascolex* sp. (undescribed) is

abundant in the upper horizons and wormholes usually penetrate into the deeper subsoil (Plate II (*a*) and (*b*), and Plate III (*b*)). The depth of weathering varies with the altitude, the maximum depth (up to 5 ft.) being shown in the sub-alpine tract at about 5,500 ft. The alpine humus soil profile shows no illuvial horizons, but is essentially of the A–C type.

The physiographic diversity of the alpine and sub-alpine tracts is accompanied by some profile variations. In the upper alpine tract the alpine humus soils developing on exposed, windswept sites appear to have undergone deeper mechanical weathering, probably because of the less effective protection given by the snow, which is relatively non-persistent in these more exposed situations. Shallow variants are also fairly common, especially on wet rock surfaces (Plate II (*c*)). Other variations from the normal profile are the peaty alpine humus soils which appear to be forming from shallow humified peat (Plate II (*d*)) and the slightly gleyed version developed in association with silty bog soils and gley podzols (Plate III (*b*)).

Typical profiles are described below of soils of this group developed on gneissic granite and phyllite at Kosciusko, and on basalt at Kiandra.

Alpine humus soil (*Profile No. C. 21*)

Environment: alpine tract, near headwaters of Snowy River, Kosciusko; 6,370 ft. elevation; steep, north-easterly aspect; free drainage; parent-rock material gneissic granite; tall alpine herbfield vegetation of *Celmisia longifolia–Poa caespitosa* alliance; average annual precipitation about 82 in., with heavy winter snow.

A_0, 0–3 in. Brown, semi-humified organic matter, consisting mainly of roots and leaves of the grass *Poa caespitosa*; finely laminated at surface, but becoming structureless near mergence with A_1; porous, mellow; slightly moist.

A_1, 3–14 in. Brownish-black sandy loam, merging with A_2; quartz gravel and small flakes of biotite fairly common; fine crumb structure; porous, friable; humus and grass roots abundant; moist; earthworms fairly common.

A_2, 14–22 in. Brownish-black gritty loam, merging with A_3C; decomposing stones of granite, quartz gravel, and small flakes of biotite plentiful; crumb structure; porous, friable; humus and grass roots abundant; moist; occasional worm-tracks.

A_3C, 22–28 in. Dark yellowish-brown gritty loam, passing into rotten rock; stones of decomposing granite and small flakes of biotite plentiful; almost single-grain structure; closed, compact to slightly indurated; little humus and few grass roots; moist; very occasional earthworm tracks.

Alpine humus soil (*Profile No. C. 1*)

Environment: lower sub-alpine tract, near Hotel Kosciusko; 5,010 ft. elevation; steep, easterly aspect; free drainage; parent-rock material gneissic granite; sub-alpine woodland vegetation of *Eucalyptus niphophila* alliance; average annual precipitation 49 in., with moderate winter snow.

A_0, 0–2 in. Dark grey, semi-humified grass litter of *Poa caespitosa*; finely laminated near surface, becoming structureless near mergence with A_1; open, mellow to friable; slightly moist.

A_1, 2–12 in. Dark brownish-grey sandy loam, merging with A_2; quartz gravel and small flakes of biotite fairly common; medium crumb structure; porous, friable; humus and grass roots abundant; moist; earthworms and small black ants common.

A_2, 12–25 in. Brownish-grey sandy loam, merging with A_3; quartz gravel and small flakes of biotite fairly common; fine to medium crumb structure; fine porous, fairly friable; humus and grass roots plentiful; slightly moist; occasional earthworms.

A_3, 25–36 in. Brownish-yellow gritty loam, passing gradually into stony A_4C horizon and thence into decomposing granite; occasional stones of rotten granite, small flakes of biotite common; fine crumb to single-grain structure; fine porous to closed, slightly compact; little humus and few roots; almost dry; occasional worm-tracks.

Alpine humus soil (*Profile No. S. 18*). (Plate III (*a*))

Environment: alpine tract, near Rawson Pass, Kosciusko; 6,800 ft. elevation; moderate slope, northerly aspect; free to slightly impeded drainage; parent-rock material phyllite; tall alpine herbfield vegetation of *Celmisia longifolia–Poa caespitosa* alliance; average annual precipitation about 85 in., with heavy winter snow.

A_0, 0–4 in. Dark brown, semi-humified organic matter, consisting mainly of grass litter; finely laminated near surface, but structureless near mergence with A_1; porous, mellow; moist.

A_1, 4–8 in. Dark greyish-brown silty loam, merging with A_2; small fragments of phyllite fairly common; very fine crumb structure; fine porous, friable to slightly compact; humus and grass roots abundant; moist, earthworms fairly common.

A_2, 8–14 in. Greyish-brown silty loam, merging with A_3C; larger fragments of phyllite common; very fine crumb structure; very fine porous, friable to compact; humus and grass roots plentiful; moist; occasional earthworms.

A_2C, 14–24 in. Yellowish-brown gritty loam, passing into rotten phyllite; stones of phyllite abundant; almost single-grain structure; almost closed, compact; very little humus and few roots; damp; earthworms not observed.

Alpine humus soil (*Profile No. N. 47*)

Environment: sub-alpine tract, Bullock Hill, near Kiandra; elevation approximately 5,000 ft.; moderate slope, northerly aspect; fairly free drainage; parent-rock material basalt; sub-alpine woodland vegetation of *Eucalyptus niphophila* alliance; average annual precipitation about 60 in. with moderate winter snow.

A_0, 0–½ in. Brown, semi-humified grass litter of *Poa caespitosa*, merging into A_1; porous ,friable, damp.

A_1, ½–5 in. Dark brownish-black clay loam, merging with A_2; crumb structure; porous, friable; humus and grass roots very abundant; damp; earthworms, white curl grubs, and small black ants plentiful.

A_2, 5–10 in. Brownish-black clay loam, merging with A_3; crumb structure; fine porous, slightly friable; humus and roots abundant; damp; earthworms, white curl grubs, and small black ants plentiful.

A_3, 10–14 in. Yellowish-brown clay loam, merging into A_4C; rotten basalt stones fairly common; loose crumb structure; almost closed, slightly compact; humus and roots moderate in amount; damp; occasional earthworms and white curl grubs.

A_4C, 14–20 in. Brownish-yellow stony loam; passing into decomposing basalt below 20 in.; rotten basalt stones abundant; structureless; closed, compact; little humus and few roots; almost wet; no fauna observed.

Analytical data

The mechanical composition, organic-matter content, pH and silica-sesquioxide ratio of the clay of representative profiles of alpine humus soils on several rocks are given in Table 1.

TABLE I

Profile number	*C. 15*				*K. 4*			*S. 18*				*C. 19*				*C. 21*			
Elevation (ft.)	*7,275*				*7,050*			*6,800*				*6,630*				*6,370*			
Parent material	*Gneissic granite*				*Gneissic granite*			*Phyllite*				*Gneissic granite*				*Gneissic granite*			
Vegetation	*Tall alpine herbfield*				*Tall alpine herbfield*			*Tall alpine herbfield*				*Tall alpine herbfield*				*Tall alpine herbfield*			
Horizon	A_0	A_1	A_2	A_3C	A_0	A_1	A_2C	A_0	A_1	A_2	A_3C	A_0	A_1	A_2	A_3C	A_0	A_1	A_2	A_3C
Depth (in.)	0–2	2–15	15–20	20–35	0–4	4–13	13–25	0–4	4–8	8–14	14–24	0–3	3–13	13–17	17–27	0–3	3–14	14–22	22–28
Colour*	..	Benzo-brown	Light-drab	Pinkish-buff	Benzo-brown	Fuscous	Wood-brown	..	Dresden brown	Cinnamon-brown	Yellow ochre	Buffy-brown	Benzo-brown	Saccardo's umber	Wood-brown	..	Benzo-brown	Benzo-brown	Light-drab
Stones and gravel	..	17·0	57·2	38·6	2·8	0·3	58·9	..	20·6	61·7	64·1	4·2	10·2	46·1	50·3	..	12·1	59·9†	48·2
Composition of oven-dry fine earth																			
Total sand	..	64·1	70·4	75·9	53·6	46·8	69·0	..	58·5	61·0	73·7	..	61·4	64·0	73·0	..	57·5	62·5	63·5
Silt	..	8·2	9·4	11·3	8·7	10·9	12·5	..	14·4	17·3	18·2	..	10·2	8·5	5·7	..	12·4	12·1	18·0
Clay	..	21·3	16·7	11·6	21·4	27·0	15·4	..	21·0	18·1	6·9	..	22·1	22·7	20·0	..	23·8	19·5	15·6
Organic matter‡	..	6·4	3·5	1·2	16·3	15·3	3·1	..	6·1	3·6	1·2	24·8	6·3	4·8	1·4	..	6·3	5·9	2·9
pH	..	4·2	4·6	4·9	4·0	4·2	4·6	..	4·5	4·6	4·8	4·1	4·4	4·5	4·9	..	4·8	4·8	5·2
Silica-sesquioxide ratio of clay	..	2·0	2·0	1·6	..	..	..	..	1·5	1·9	2·7	..	3·1	2·4	2·0	..	1·5	1·8	1·9

TABLE 1 (*cont.*)

Profile number	*CS. 3*					*C. 5*				*C. 4*				*C. 1*				*N. 47*				
Elevation (ft.)	*6,300*					*5,950*				*5,700*				*5,010*				*c. 5,000*				
Parent material	*Gneissic granite*					*Gneissic granite*				*Gneissic granite*				*Gneissic granite*				*Basalt*				
Vegetation	*Tall alpine herbfield*					*Sub-alpine woodland*				*Sub-alpine woodland*				*Sub-alpine woodland*				*Sub-alpine woodland*				
Horizon	A_0	A_1	A_2	A_3	A_4C	A_0	A_1	A_2	A_3	A_0	A_1	A_2	A_3	A_0	A_1	A_2	A_3	A_0	A_1	A_2	A_3	A_4C
Depth (in.)	0–4	4–10	10–18	18–25	25–31	0–4	4–9	9–14	14–19	0–5	5–12	12–20	20–36	0–2	2–12	12–25	25–36	0–½	½–5	5–10	10–14	14–20
Colour*	Benzo-brown	Benzo-brown	Buffy-brown	Buffy-brown	Wood brown	..	Benzo-brown	Saccardo's umber	Light-drab	Benzo-brown	Benzo-brown	Dresden-brown	Wood-brown	..	Benzo-brown	Benzo-brown	Buffy-brown	..	Fuscous	Bister	Snuff-brown	Snuff-brown
Stones and gravel	0·9	4·4	11·6	27·1	2·3	..	20·8	38·0	44·7	0·0	12·9	28·1	44·5	..	12·9	6·6	19·5	..	..	..	..	..
Composition of oven-dry fine earth																						
Total sand	..	42·4	55·9	57·4	55·5	..	47·0	49·6	62·4	..	37·0	42·8	54·8	..	45·6	48·5	55·3	..	24·9	28·8	35·4	39·1
Silt	..	11·5	16·6	14·7	18·9	..	12·0	15·2	15·3	..	13·9	15·8	23·9	..	11·9	15·8	19·2	..	22·6	26·5	24·4	21·8
Clay	..	39·4	22·0	22·0	22·0	..	30·6	27·5	19·2	..	36·8	33·3	18·5	..	31·6	28·5	22·5	..	39·0	35·9	35·3	34·8
Organic matter‡	27·6	12·7	5·5	5·4	3·6	..	10·4	7·7	3·1	23·9	12·3	8·1	2·8	..	10·9	7·2	3·0	..	14·1	8·8	5·0	4·3
pH	5·4	5·0	5·2	5·3	5·4	..	4·5	4·8	5·1	4·6	4·7	4·9	5·0	..	4·9	5·0	5·2	..	4·9	4·8	5·1	5·1
Silica-sesquioxide ratio of clay	..	..	..	..	..	..	1·1	1·0	1·0	..	1·9	1·4	3·1	..	1·2	1·3	3·3	..	..	..	..	..

* Colours according to Ridgway's Colour Atlas.
† The higher figures occasionally encountered for stone and gravel in intermediate horizons are where these horizons included a stone line.
‡ Calculated from organic carbon (Walkley-Black method).

These data show that the organic matter, which is very high in the surface soils, persists at a relatively high level to considerable depths. The soils are extremely acid in the upper horizons, usually lower than pH 5·0 in the A_1, and showing a rise into the decomposing rock.

The mechanical-composition figures show that stones and gravel increases markedly with depth, as does the sand fraction of the fine earth, but the clay content is distinctly higher in the topsoil than in the lower horizons.

Although the silica-sesquioxide ratio of the clay fraction falls slightly into the subsoil in some profiles, it remains constant or rises in others, whilst the free-ferric-oxide figures (Table 4) give no suggestion of sesquioxide migration.

In view of the high rainfall, the absence of podzolization is striking, since at lower altitudes on the Kosciusko massif on the same rock, gneissic granite, podzolized soils are normally developed, although receiving lower annual precipitations. This, together with changes in the internal properties of the alpine humus soils with altitude, will be referred to later.

For four profiles developed on gneissic granite the exchange capacity and the exchangeable cations have been determined (Table 2).

The exchange capacities,[1] which are moderate in the topsoil, decrease markedly down the profile to very low values. They are related mainly to the organic-matter content of the soil. This is illustrated by the fact that the exchange capacities of the topsoils vary in accordance with their organic-matter content, and by the relative uniformity in the subsoils in which the organic-matter content is low. The comparative lack of relationship between exchange capacity and clay content reflects the composition of the clay, which consists largely of kaolinite and clay biotite, the latter in relatively coarse subdivision.

The exchange complex is highly base-unsaturated, the proportion of exchangeable bases being low. This is noteworthy in view of the absence of podzolization. The strong acidity of the alpine humus soils at Kosciusko is probably due to the presence of a large proportion of exchangeable aluminium (with some iron) on the exchange complex of the clay, and to the hydrogen ions released from the humic acids of the organic matter. Evidence for the presence of exchangeable aluminium is presented later.

The ability of these soils to support the vigorous growth of herbaceous vegetation that they do, especially of snow grass (*Poa caespitosa*), would not be anticipated from their low content of exchangeable bases.

This and other evidence suggests that the vigour of plant growth at Kosciusko is made possible by a rapid circulation of the limited base capital by the decomposition of the vegetation and earthworm activity.

[1] The method used, involving saturation with the ammonium ion, removal of excess ammonium acetate with 60 per cent. alcohol, and subsequent replacement of the adsorbed ammonium by distillation with magnesium oxide, gives with these soils results which are too low, since part of the ammonium-saturated organic matter is removed by the alcohol treatment.

TABLE 2

Exchange Capacity and Exchangeable Cations of some Alpine Humus Soils formed on Granite (in m.e./100 g.)

Profile No.	*16*					*C. 19*			*CS. 3*				*CS. 4*			
Horizon	A_0	A_1	A_2	A_3C	C	A_1	A_2	A_3C	A_0	A_1	A_2	A_3C	A_0	A_1	A_2	A_3C
Depth . .	0–9″	9–17″	17–24″	24–36″	36–48″	3–13″	13–17″	17–27″	0–4″	4–10″	10–18″	18–25″	0–7″	7–21″	21–30″	30–40″
Ex. capacity . .	13·71	10·91	6·07	7·93	5·47	9·00	8·18	4·64	27·87	17·12	10·49	10·69	16·36	17·08	12·21	4·99
Ex. Ca. . .	0·47	0·47	0·41	0·71	0·90	0·57	0·70	0·49	12·18	3·05	0·57	0·58	4·09	1·77	0·83	0·66
Ex. Mg . .	2·20	0·88	0·56	0·64	0·32	1·28	1·08	1·86	3·08	5·98	1·86	2·14	0·98	0·16	3·24	1·20
Ex. K . .	tr.	..	..	..	..	0·12	0·10	0·05	1·89	0·79	0·12	tr.	0·37	0·19	tr.	tr.
Ex. Na . .	0·00	..	..	..	..	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00

This view is supported by the higher contents of exchangeable bases in the organic horizons of profiles CS. 3 and CS. 4.

Contributory or alternative sources for mineral nutrients might be the fine fragments of rock material which release bases to the plant roots either directly by contact exchange or indirectly by solution and subsequent uptake from the groundwaters.

Relationships with Associated Soils

The most important topographic and climatic relationships of alpine humus soils with other soil groups are considered below.

Topographic sequences

The catena[1] which is most commonly developed on gneissic granite, as for example near Mt. Townsend in the alpine tract on Kosciusko, is as follows: Alpine humus soils (tall alpine herbfield and sod-tussock

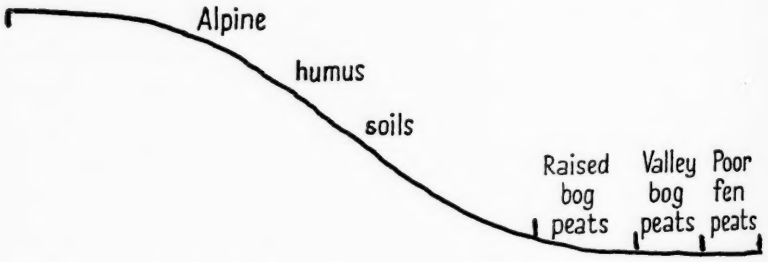

FIG. 2. Topographic sequence, Mt. Townsend.

grassland vegetation) on all freely drained upper, middle, and lower slopes, with raised bog peats (raised bog) on the wet lowest slopes, and on wet situations on the flat valley bog peats (valley bog) and poor fen peats (fen) in strongly acid and acid situations respectively (Fig. 2).

The above catena develops where the water-table on the flat is at or near surface-level for most of the year.

Where the level of the water-table is not so high (as near Bett's Camp in the sub-alpine tract) the corresponding sequence is alpine humus soils on all freely drained slopes (as above), with gley podzol (sod-tussock grassland) on the moist lower slopes, and with silty bog soil (sod-tussock grassland) and occasionally poor fen peat (fen) on the lowest slopes and flats (Fig. 3).

These lower water-table conditions may be associated with one of three changes: (*a*) a direct decrease in annual precipitation; (*b*) improved drainage due to deeper entrenchment of the associated watercourse; or (*c*) a reduction in the ratio between the area of catchment and the area receiving the run-off from it.

[1] The associated vegetation is indicated in brackets.

A most interesting topographically controlled micro-climatic sequence occurs on gneissic granite on the lower sub-alpine and upper montane tracts of the north-western Monaro, where broad valleys are strongly affected by cold-air drainage. Under these conditions the coldest parts of the catena are at the top and bottom of the slope and the warmest part in the middle. Thus the sequence of soils, as observed near Boggy

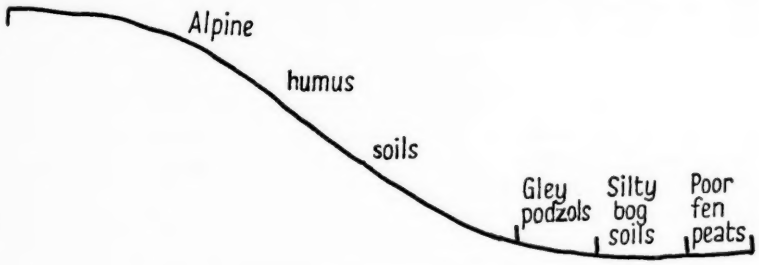

FIG. 3. Topographic sequence, Bett's Camp.

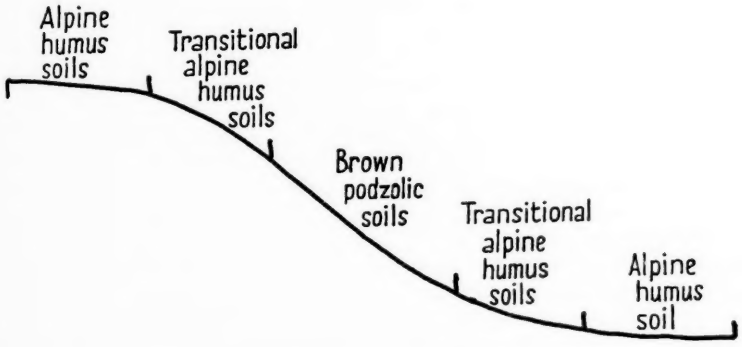

FIG. 4. Topo-climatic sequence, Boggy Plains.

Plains, Tantangara, Long Plain, and Gurrangorambla within a vertical distance of as little as 300 ft., is alpine humus soil (sub-alpine woodland and sod-tussock grassland) on the cold top of the slope; transitional alpine humus soil (wet sclerophyll forest) on the cool upper slopes; brown podzolic soil (wet sclerophyll forest) on the warmest middle slopes; transitional alpine humus soil (wet sclerophyll forest) on the cool lower slopes, and alpine humus soil (sod-tussock grassland and sub-alpine woodland) on the cold valley floor (Fig. 4).

In locally wetter sites the alpine humus soils are replaced by gley podzols, silty bog soils, or fen or bog peats.

All the above sequences are also developed on slate and basalt.

Climatic or altitudinal sequences

Within a horizontal distance of about 20 miles, the elevation decreases from 7,328 ft. in the upper alpine tract at Mt. Kosciusko to about 3,000 ft. in the lower montane tract near the junction of the Thredbo and Snowy rivers. This is accompanied by a decrease in average annual precipitation from about 90 in. including abundant winter snow, to 22 in. with but little snow. Over the same distance normal mean annual temperature increases from 36° F. at the summit to 54° F. at 3,000 ft.

Since all factors other than climate can be held constant throughout this range, this altitudinal succession provides an opportunity to study the effects of wide climatic variations on soil formation on acid rocks (gneissic granite) over the lower temperature ranges and the relation of the alpine humus soils to other great soil groups. In the present study, therefore, an altitudinal sequence of soil sites was chosen for which all pedogenic factors except climate were approximately the same: the soils being developed *in situ* on gneissic granite, apparently during a similar interval of post-glacial time, under the influence of the same conditions of drainage and the same regional flora and fauna (as distinct from plant and animal communities).

The effect of such climatic variations on soil formation on a basic rock (basalt), under otherwise constant factor conditions, has been considered in the previous paper (Hallsworth, Costin, *et al.*, 1951).

In most soil property-elevation relationships worked out in other countries (e.g. Jenny, 1941) the soil property is shown to vary in the same direction with increasing altitude. This is probably due to the limited altitudinal range encountered. If the sequence is wide enough to extend from the relatively warm sub-humid climate (of the Monaro Tablelands) to a cold wet alpine climate, the maximum in most soil properties is more likely to occur at some intermediate zone rather than at either altitudinal extreme. At the lower extreme, soil-forming processes are limited by insufficient moisture and at the upper extreme by inadequate temperatures. From the results presented below it appears that the optimum combination at Kosciusko occurs in the upper sub-alpine tract between about 5,500 ft. and 6,000 ft. Above 6,000 ft. pedogenesis is limited by low temperatures and physical weathering processes predominate. Below 5,000 ft., on the other hand, pedogenesis is limited increasingly by inadequate moisture.

On ascending the Kosciusko plateau from the lower eastern montane tract at 3,000 ft., the sequence of great soil groups and associated plant communities is as follows: iron podzols (with vegetation of dry sclerophyll forest and wet sclerophyll forest) between 3,000 and 4,250 ft., brown podzolic soils (wet sclerophyll forest) between 4,250 ft. and 4,750 ft., transitional alpine humus soils (wet sclerophyll forest) between 4,750 ft. and the level of the winter snow line at 5,000 ft., and alpine humus soils above this level (sub-alpine woodland in the sub-alpine tract between 5,000 ft. and 6,000 ft., and tall alpine herbfield in the alpine tract above 6,000 ft.).

The iron podzols at 3,000 ft. are replaced at lower levels on the Monaro

Tableland proper by grey-brown podzolic soils (savannah woodland and dry-tussock grassland), and the latter by brown soils of light texture (dry-tussock grassland) as progressively drier conditions are encountered towards the rain-shadow areas of the central Monaro.

The corresponding variations in soil properties between 3,000 and 7,328 ft. are illustrated in Figs. 5 to 13.

Depth of weathering and horizon development. The relationship between altitude and depth of weathering and horizon development are summarized in Fig. 5.

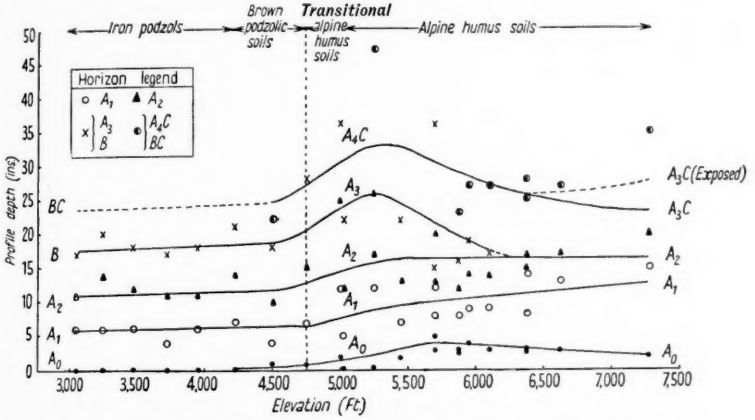

FIG. 5. Relationship between altitude and soil profile development.

Attention may be drawn at this stage to the essential differences between the horizon development of the iron podzols and brown podzolics on the one hand, and the transitional alpine humus and alpine humus soils on the other. The profile of the podzolized soils invariably shows an illuvial B horizon of sesquioxides. As the brown podzolic soils are replaced by transitional alpine humus soils, however, eluviation of sesquioxides gradually ceases, until in the alpine humus soils no zone of sesquioxide deposition occurs.

For this reason the horizons shown in Fig. 5 and subsequent figures are designated A_0, A_1, A_2, A_3, or A_3C, and sometimes A_4C in the upper zone (above 4,750 ft.), and A_0 (sometimes), A_1, A_2, B, and BC in the lower zone.

The soil-profile depth is least in the montane tract, increases suddenly above the lower limit of the sub-alpine tract (5,000 ft.) to a maximum in the upper sub-alpine tract (about 5,500 ft.), and declines again in the alpine tract. Exposed upper alpine situations, however, may have abnormally deep soil profiles due to extreme penetration and weathering by frost.

Below 4,250 ft. the A_0 horizon is virtually lacking. It shows its best development near the upper limit of the sub-alpine tract, from which it decreases slightly at higher altitudes. Its absence from lower levels may

be attributed to the limitation in organic matter production by insufficient moisture. Although at progressively higher levels the rate of decomposition of organic matter decreases, the thickness of the A_0 horizon increases only to the upper limit of the sub-alpine tract above which production of organic matter is progressively restricted by lower temperatures.

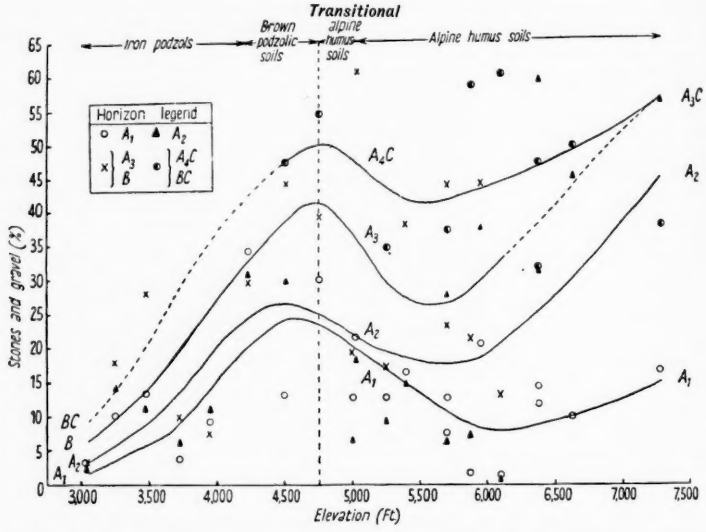

FIG. 6. Relationship between altitude and amount of stones and gravel.

It might be noted that in the shallower profiles of the alpine tract the organic matter usually penetrates to the decomposing parent material, whereas in the deeper sub-alpine profiles there is a layer of mineral soil underlying the organo-mineral horizons.

Stones and gravel (> 2 mm.). The relationship between altitude and the amount of stones and gravel is shown in Fig. 6.

These fractions are present in greatest quantities in the alpine humus soils of the alpine tract, and in smallest quantitites in those of the sub-alpine tract. A secondary maximum occurs in the transitional alpine humus soils of the upper montane tract situated just below the winter snow line, from which there is a progressive decrease to lower montane levels.

Coarse sand (2–0·05 mm.). Fig. 7 illustrates the relationship between altitude and the quantity of coarse sand.

The amount of coarse sand is greatest in the montane tract and at a slightly lower level in the alpine tract. Between these elevations the coarse sand falls to a minimum in the sub-alpine tract.

Fine sand (0·05–0·02 mm.). Fig. 8 illustrates the relationship between altitude and the quantity of fine sand.

This relationship is almost the reverse of that for coarse sand, with a maximum occurring in the sub-alpine tract and the remainder of the soils above and below being relatively uniform in their fine sand content.

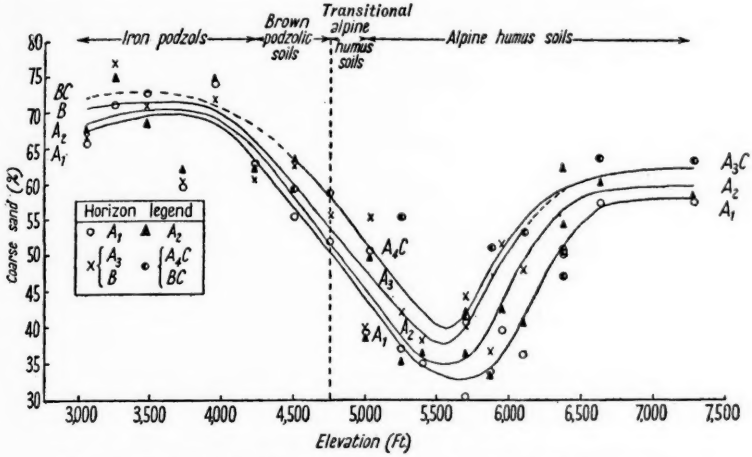

FIG. 7. Relationship between altitude and amount of coarse sand.

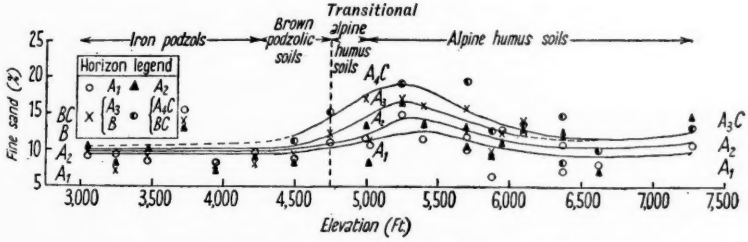

FIG. 8. Relationship between altitude and amount of fine sand.

Silt (0·02–0·002 mm.). Fig. 9 illustrates the relationship between altitude and the quantity of silt.

A distinct maximum occurs in the sub-alpine tract, from which the quantity of silt falls gradually with decreasing elevation in the montane tract, and sharply with increasing altitude in the alpine tract.

Clay (< 0·002 mm.). In the clay sequence (Fig. 10) the maximum again occurs in the sub-alpine tract from which the amount of clay falls sharply towards the upper limit of the alpine tract and more gradually towards the lower limit of the montane tract.

The greatest difference between the clay contents of successive horizons in the profile occur in the alpine and sub-alpine tracts (i.e. in the alpine humus soils) and progressively less in the montane tract in the transitional alpine humus, the brown podzolics, and the iron podzols.

It might be noted here that the podzolized soils, although showing distinct eluviation of sesquioxides, do not contain an illuvial horizon of clay.

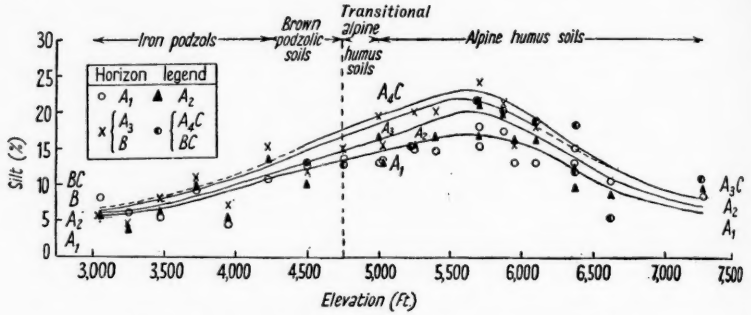

FIG. 9. Relationship between altitude and amount of silt.

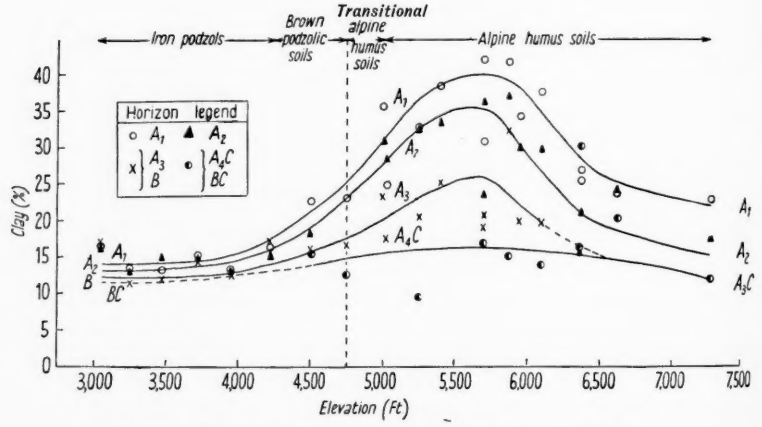

FIG. 10. Relationship between altitude and amount of clay.

Organic carbon. The organic carbon sequence (Fig. 11) approximates to that for clay, the maximum occurring in sub-alpine tract, rather less in the alpine tract, with distinctly lower figures in the montane tract.

This sequence is at variance with the findings of certain other workers who have emphasized the progressive increase in organic carbon content with altitude. The amount of organic carbon in a soil is a balance between the rate of production and the rate of oxidation of organic matter. At lower, warmer, and drier levels much of the little organic matter produced is oxidized. Increases in altitude are usually accompanied by higher precipitations and lower temperatures, the former increasing the production of organic matter providing temperature is not limiting, and the latter retarding its oxidation. With still greater increases in altitude,

however, as in the alpine tract at Kosciusko, low temperatures limit plant growth to such an extent that, irrespective of increasing precipitation, the production of organic matter is curtailed more than its rate of oxidation, and a decline in the organic carbon content of the soil at higher altitudes takes place.

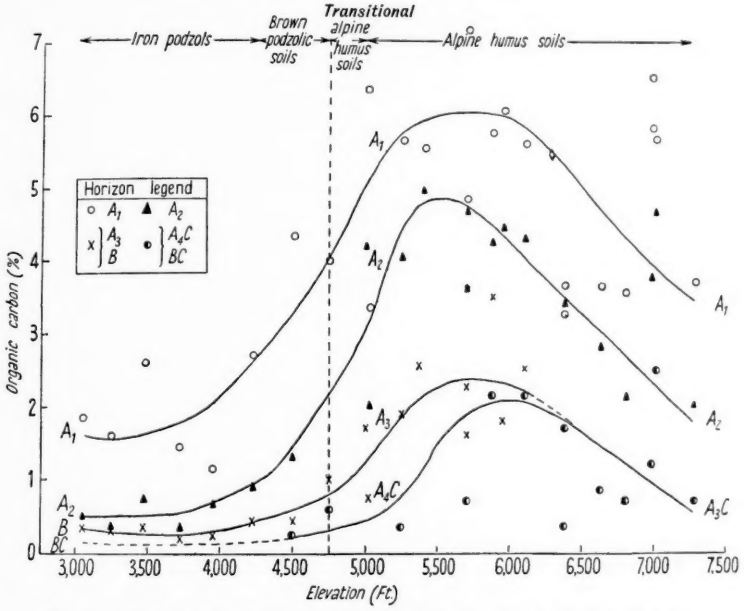

FIG. 11. Relationship between altitude and amount of organic carbon.

Hydrogen-ion concentration. The sequence of hydrogen-ion concentration (Fig. 12) differs from all others studied in increasing steadily from a minimum in the montane tract to a maximum in the alpine tract. This suggests that, within the range of climatic conditions encountered at Kosciusko, increasing moisture and decreasing temperature both operate in the same direction in their effect on soil acidity.

In view of the following discussion on the sequences for the chemical composition of the clay fraction, it is interesting to note that the processes of podzolization are not necessarily related to soil acidity, since the most podzolized soils occur in the montane tract under the least acid conditions and the unpodzolized soils in the sub-alpine and alpine tracts under conditions of stronger acidity.

Chemical composition of the clay fraction. Determinations have been made of the silica, titanium-dioxide, alumina, and ferric-oxide contents of all profiles studied in the above sequence, but since silica showed little variation in the different profiles, whilst the variations of the other components were generally similar, graphical presentation of the data has

been restricted to the silica-sesquioxide ratio, which effectively summarizes all these data (Fig. 13).

Little altitudinal variation was found in the amount of silica except for a slight minimum in the soils of the sub-alpine tract. The titanium-dioxide sequence also showed little variation, but in contrast to the silica sequence, a slight maximum occurred in the sub-alpine tract.

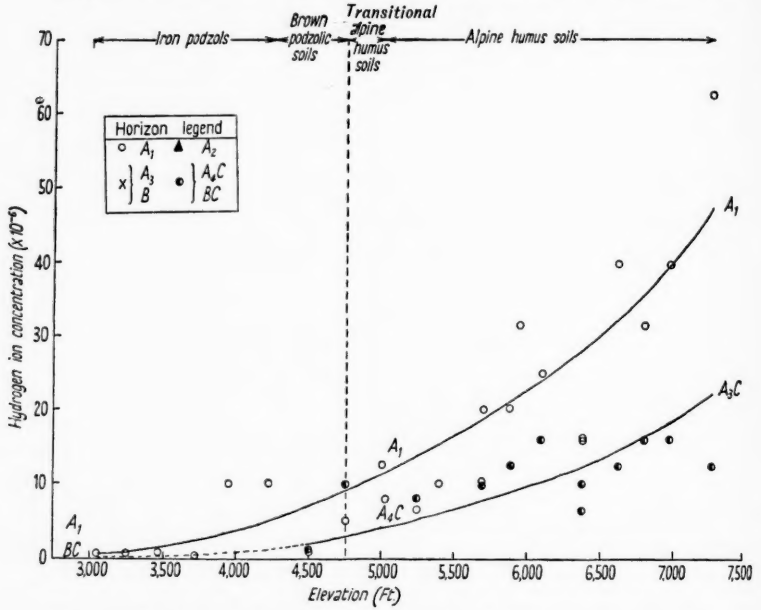

FIG. 12. Relationship between altitude and hydrogen-ion concentration.

Alumina showed a broad maximum in the alpine and sub-alpine tracts from which it declined suddenly in the montane tract.

The ferric-oxide sequence resembles the alumina sequence, except that at higher altitudes ferric oxide decreases, and at lower altitudes increases, down the profile.

Considering the profiles as a whole, the silica-sesquioxide ratios show a distinct minimum in the upper sub-alpine tract from which they rise slightly in the alpine tract and considerably into the montane tract. Since the silica content of the clay fraction remains relatively constant at all altitudes, Fig. 13 reflects the relatively greater accumulation of sesquioxides in the alpine humus soils than in the podzolized soils of the montane tract.

The variations of the silica-sesquioxide ratio within the profiles shown in the above sequence do not in themselves provide evidence of podzolization; indeed, in the alpine humus soils which are not podzolized, the ratio is generally slightly less in the subsoil than in the topsoil, but in the distinctly podzolized soils of the montane tract the reverse is the case.

In order to investigate this point further, determination of the free ferric oxide (Deb, 1950) of the clay fraction was made on certain profiles.

The ferric-oxide content for the entire profiles reflects the same trend as shown by Fig. 13, namely, that the content of sesquioxides is greatest in the alpine humus soils of the sub-alpine tract, slightly less in the alpine

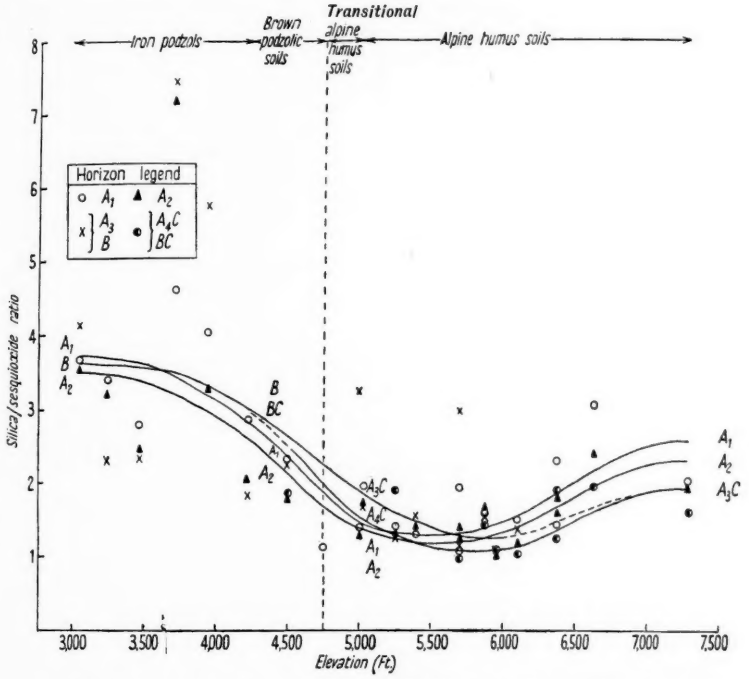

FIG. 13. Relationship between altitude and ratio of silica to sesquioxides.

humus soils of the alpine tract, and least in the podzolized soils of the montane tract.

On the other hand, the variation in ferric-oxide content down the profile is not related to the silica-sesquioxide ratio. That translocation of sesquioxides has occurred in the podzolized soils is shown by the accumulation of ferric oxide at some depth in the subsoil. In the alpine humus soils, however, the content of free ferric oxide is approximately uniform in the profile or tends to a maximum in the topsoil.

The mineralogy of the clay fraction

The clays from certain profiles were examined by X-ray diffraction technique (MacEwan, 1946).

TABLE 3

Free Ferric-oxide Content

Elevation (ft.)	*Soil group*	*Profile and soil number*	*Depth (in.)*	$\%Fe_2O_3$
7,275	Alpine humus soil	C. 15·2	15–20	1·9
		C. 15·3	20–35	2·3
6,630	,, ,, ,,	C. 19·1	3–13	1·9
		C. 19·2	13–17	2·1
		C. 19·3	17–27	2·1
6,370	,, ,, ,,	C. 21·1	3–14	2·8
5,950	,, ,, ,,	C. 5·1	4–9	3·7
		C. 5·2	9–14	2·1
		C. 5·3	14–19	3·1
5,700	,, ,, ,,	C. 4·1	5–12	3·3
		C. 4·2	12–20	2·9
		C. 4·3	20–36	2·8
5,020	Transitional alpine humus soil	C. 6·1	¼–5	2·0
		C. 6·2	5–12	2·5
		C. 6·3	12–22	2·1
4,230	Iron podzol	C. 9·1	0–7	1·8
		C. 9·2	7–14	2·7
		C. 9·3	14–20	1·5
3,470	,, ,,	C. 12·2	6–12	1·2
		C. 12·3	12–18	1·8
3,050	,, ,,	C. 14·1	0–6	1·8
		C. 14·2	6–11	2·2
		C. 14·3	11–15	2·9

From consideration of this and the foregoing data, the soils may be subdivided into three groups:

(*a*) The alpine humus soils above 6,000 ft.
(*b*) The alpine humus soils below 6,000 ft.
(*c*) The podzolized soils below 4,500 ft.

The clays of the alpine humus soils above 6,000 ft. show a silica-sesquioxide ratio which rarely falls below 2·0 and a free ferric-oxide content of approximately 2·0 per cent. From the intensity of the lines of the X-ray photographs, the clay fraction appears to be largely clay biotite (up to 75 per cent.) with between 10 and 40 per cent. kaolinite and a little free hydrated aluminium oxide, probably gibbsite.

Below 6,000 ft. the alpine humus soils show a lower silica-sesquioxide ratio, which is here always below 2·0 and a free ferric-oxide content of between 2 and 3 per cent. The same minerals are present, kaolinite forming about 25 per cent., but the clay biotite is distinctly lower and the free aluminium oxide higher.

Below 4,500 ft. podzolized soils are formed, which show a silica-sesquioxide ratio higher than 2·0, and although this ratio shows no lowering in the B horizon, there is a demonstrable accumulation of free ferric oxide. Kaolinite again appears to form about one-quarter of the clay minerals and clay biotite most of the rest.

A little quartz is present in all three groups.

The quantity of kaolinite present was calculated by comparison with X-ray diffraction photographs of known mixtures and by differential thermal curves for three samples.

The kaolinite may have two origins. It may have formed *in situ* from the decomposition of felspar of the parent rock or it may have been wind-deposited. In support of the latter, it was found that the clay fraction of a snow-patch meadow soil, which would receive a greater proportion of wind-blown material, by virtue of the concentrating effect of the snow-patch, showed a much greater amount of kaolinite than the other soils, as judged by the relative intensities of the lines in the X-ray diffraction photograph.

The clay biotite appears to be formed by the disintegration of biotite, which is present in abundance in the sand fraction and in the parent granite. The presence of gibbsite is indicated by the presence of a 5Å line in X-ray photographs and of an endothermic peak at 340° C. in differential thermal curves. Although no attempt was made to determine gibbsite quantitatively, it is noteworthy that sample C. 5·1 (from 5,950 ft.) showed the greatest peak at 340° C., sample C. 19·2 from 6,620 ft. showed a much smaller peak, and sample C. 14·1 from the podzol zone at 3,050 ft. showed no peak at all at this temperature.

The occurrence of the gibbsite seems to be confined to the alpine humus soils and to occur in greatest amount around 5,500 ft., at which altitude the alpine humus profile is about at its maximum development. Its origin is discussed subsequently.

TABLE 4

Sample No.	*Elevation (ft.)*	SiO_2/R_2O_3	*Intensity of 5Å line*	*% loss on ignition*
$19A_2$	6,630	2·06	medium weak	12·9
5B	5,950	0·94	medium	23·8
$5A_3$	5,700	1·97	medium weak	19·48
$6A_1$	5,020	1·95	,, ,,	11·50
12B	3,470	2·20	very weak	9·07
$14A_1$	3050	2·30	absent	12·42

Colour. An aspect of soil colour which has given rise to some discussion is the redness shown by permanently moist but not water-logged subsoils. At least in the alpine humus and transitional alpine humus soils at Kosciusko, this characteristic red colour is attributed to the permanent existence of ferric oxide as a colloidal solution. It is significant in this regard that the red colour is not a feature of the lower montane soils or of the upper alpine soils of exposed situations. At the former elevation permanently moist subsoil conditions do not obtain, and at the latter elevation deep freezing and thawing of the soil moisture results in a comparable condition of dryness. In neither instance would the permanent existence of a colloidal solution of ferric hydroxide be favoured.

This characteristic red colour differs distinctively from the red colour

developed in the arid and semi-arid soils of this State, which is due apparently to the irreversible precipitation of ferric oxide on the surface of the coarser mineral particles or its crystallization into separate minerals such as haematite, ilmenite, &c.

Discussion

From the foregoing altitudinal sequences it can be seen that several soil properties obtain the optimum development in the alpine humus soils of the upper sub-alpine tract.

The particle-size distribution of the soils, which is a function of both physical and chemical weathering, can be related to differences in the degree of these processes.

Physical weathering is of major importance in the production of the coarser fractions and chemical weathering in the production of the finer fractions. Provided there is no considerable gain or loss of soil material by surface erosion, the quantity of coarser and finer materials in any soil profile represents a balance between the production of larger particles by physical weathering and their breakdown to finer particles by chemical processes. This approach provides a means of establishing with some precision the particle sizes at which physical weathering virtually ceases and chemical weathering becomes dominant.

Applying this to the sequences obtained at Kosciusko, the greater proportions of stones and gravel in the soils of the alpine tract are attributable to the more vigorous frost weathering of rocks at these elevations. The slightly lower quantities of stones and gravel in the alpine humus soils of the sub-alpine tract are in accordance with the less severe mechanical weathering experienced. The slight secondary maximum of the transitional alpine humus soils of the upper montane tract is interesting in view of the abnormally severe frost action and temperature fluctuations associated with the continual melting and renewal of the snow cover which occur just below the winter snow-line. At lower altitudes there is a progressive decrease in the amounts of stones and gravel. This is due to the progressively smaller input of larger particles owing to the reduction in primary mechanical breakdown of the rocks, associated with the less effective penetration of frost.

That the sequence for coarse sand differs greatly from that for gravel and stones appears to reflect the variations in the relative importance of physical and chemical weathering at different elevations. Slightly greater quantities of coarse sand than of stones and gravel are present in the alpine humus soils of the alpine tract, but in the sub-alpine tract the proportion of coarse sand to the larger fractions diminishes sharply. This trend is completely reversed in the montane tract, where the proportion of coarse sand first equals and then far exceeds the proportions of stones and gravel.

In striking contrast to the sequence for coarse sand, those for fine sand, silt, clay, and organic carbon show a definite maximum in the sub-alpine tract.

These variations may be interpreted as follows. In the alpine humus soils of the alpine tract the coarse sand fraction is high because its

production by mechanical weathering at least balances its breakdown into smaller fractions. Although moisture conditions are adequate for chemical weathering, such processes are limited by the low temperatures. In the alpine humus soils of the sub-alpine tract, however, the combination of moisture and temperature conditions appears to be more favourable to chemical weathering, as indicated by the greater proportions of silt and clay. In other words, the breakdown of the coarser sand now exceeds its rate of production from the stones and gravel. The podzolized soils of the montane tract are noteworthy for their high content of coarse sand despite their low content of stones and gravel. This accumulation of coarse sand shows that its rate of production from the stones and gravel exceeds its rate of breakdown to finer fractions. That the fine-sand sequence is the antithesis of that for coarse sand shows that the processes responsible for the production of fine sand from coarse sand are not the same as those responsible for the production of coarse sand from stones and gravel. The former appear to be dominated by chemical weathering and the latter by physical weathering. The lower moisture conditions in the montane tract limit chemical weathering, so that breakdown from coarse sand to the finer fractions is slight. A further implication of the predominance of coarse sand without a corresponding increase in fine sand is that under the conditions at Koscuisko physical weathering becomes of minor importance beyond the lower limits of the coarse-sand fraction, i.e. 0·05 mm. This lower effective limit at Koscuisko is considerably higher than that worked out by Zeuner (1949) for the frost soils of Mt. Kenya in East Africa. The latter soils contain a high percentage of particles from 0·1 to 0·01 mm. diameter, from which Zeuner concluded that the particle diameter at which frost action ceased was about 0·01 or 0·002 mm. This is obviously at variance with the findings reported here.

It is suggested that the lower size limit at which frost action ceases to be effective is not merely a function of climate, but is also related to the nature of the rock being weathered, particularly to its texture. Accordingly, the extent to which a particular rock is broken down by frost action is determined by the size of its individual particles. Although a coarse-grained rock may at first be broken down fairly rapidly into smaller fragments, further breakdown will proceed only slowly when these fragments correspond to the primary particles of the rock, such as grains of quartz, feldspar, or flakes of mica, as would be the case in granites. In contrast, a finer grained rock, such as slate, will probably be broken down more slowly at first, but the size of the fragments ultimately produced might be smaller in accordance with the smaller size of the primary particles of the parent rock. This suggestion is supported by the finer texture of the alpine humus soils derived from slate, phyllite, and basalt on the Monaro than occurs in the alpine humus soils derived from gneissic granite (Table 1). This may also be the explanation of the finer texture reported by Zeuner for the Mt. Kenya frost soils, which are developed on porphyritic lava. The large phenocrysts of anorthoclase in the lava were reported to be responsible for an irregularity in particle gradient of the soils. In accordance with the suggestion advanced above, the ultimate particles produced from these phenocrysts by frost

weathering would be larger than those produced from the ground-mass of the lava.

The occurrence of optimum conditions for chemical weathering in the sub-alpine tract is also reflected by the sequences for silt and clay which attain their maxima at these elevations. That the clay sequence exhibits the sharpest maximum is due partly to the fact that this fraction represents an end product of weathering. The fine sand and silt fractions, on the other hand, are undergoing continuous breakdown, and therefore do not accumulate to the same extent as the clay.

It is significant that the greatest differences between the clay content of successive horizons in the profile occur in the soils of the alpine and sub-alpine tracts. This is attributable on the one hand to the greater mineralization of the organic matter in the topsoils in these tracts (see later); and on the other hand to the more uniform chemical weathering of the soil profile as a whole in the montane tract due to the generally higher soil temperatures at these lower elevations and to the smaller temperature gradient from topsoil to subsoil.

Status and the Controlling Factors of the Environment

The alpine humus soils are the climatic climax soil group of the alpine and sub-alpine tracts of the Monaro region. Under conditions of pronounced cold-air drainage, as along the broad valleys of the north-western Monaro, these soils may also develop on a smaller scale in the upper montane tract as physiographic climaxes.

The essential factors of the climatic environment are a continuous ground cover of snow for at least 1 month of the year and relatively warm temperatures, combined with considerable daily temperature fluctuations during the snow-free months. Comparatively warm summers appear essential for alpine humus soil formation. This is shown by their absence from arctic and antarctic regions, which differ from alpine and sub-alpine regions mainly by their lower temperatures. Except in special cases, the soils do not freeze in winter when covered by snow, although the average atmospheric temperatures are below freezing-point. Water from the melting snow does not leach the soil as might be expected, since much of it is discharged as run-off from the dense ground cover of grass. Most of the remaining water which soaks into the soil is retained in the profile, which has an extremely high water-holding capacity due to the abundant organic matter.

The biological factor appears to be unusually important in the genesis of the alpine humus soils of the Monaro, due mainly to the role of the snowgrass (*Poa caespitosa*) and the mountain earthworm (*Megascolex*). Biologically these soils are distinguished from the podzolized soils at lower levels by the more vigorous growth of the snowgrass, and their consequently much higher organic matter contents, which, as has already been mentioned, reach a maximum in the sub-alpine tract. They are further distinguished by a correspondingly abundant and active population of earthworms. This undescribed species in the alpine humus soils frequently attains a diameter of ½ in. and a length of 9 in.

Whilst it is generally accepted that vegetation and earthworm activity may stabilize the soil by maintaining a dynamic equilibrium with regard to soil bases, their effect on the smaller mineral fractions has not been considered important. In this case, however, the growth of the snowgrass, and the subsequent mineralization of the organic matter, results in the return to the surface of appreciable quantities of colloidal material, which has been absorbed either from the soil solution or by contact exchange. To the extent to which this latter process has taken place from the coarser particles, the snowgrass is responsible for the production of colloidal clay by 'biological' weathering and its concentration in the topsoil. This is illustrated by the following analyses of snowgrass litter from Mt. Kosciusko at approximately 7,000 ft., compared with the corresponding analyses of the fine earth fraction of the underlying mineral subsoil and the unweathered parent gneissic granite (Table 5).

TABLE 5

Composition of Snowgrass Litter compared with Underlying Soil and Parent Rock

Sample	*No.*	*Depth (in.)*	*Loss on ignition* (%)	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	TiO_2 (%)	$\frac{SiO_2}{R_2O_3}$	*Clay* (%)
Litter .	C. 9·6	0–4	33·1	68·75	16·50	2·73	1·03	6·18	..
Litter .	C. 12·1	0–5	39·6	66·82	18·92	2·63	1·12	5·34	28·6
Subsoil .	C. 12·3	11–19	13·9	65·56	18·66	2·90	0·74	5·32	20·5
Subsoil .	C. 12·4	19–29	8·1	63·48	20·55	3·55	0·66	4·65	13·3
Rock .	C. 12·5	..	0·7	68·50	13·16	1·21	0·11	8·39	..

These figures indicate that a considerable amount of colloidal mineral material is being produced at the surface by decomposition of the snowgrass, which must be a factor contributing to the higher clay content which characterizes the topsoils of the alpine humus soils.

Furthermore, the mineral material thus produced is proportionately richer in sesquioxides than is the parent gneissic granite. The alumina content of the litter is so high that snowgrass at Kosciusko must be considered as an aluminium accumulator (Chenery, 1951). The gibbsite mentioned earlier as occurring in these soils most probably has originated in this manner by the following processes. In acid soils aluminium appears to be present on the exchange complex of the clay, and at acidities stronger than pH 4 as single aluminium ions (Russell, 1950). The latter low pH values would obtain at the root surfaces of the snowgrass, and aluminium would readily enter the plant. From the work of Schofield (Russell, 1950) it would appear that the aluminium ions, on entering a slightly less acid environment (as would occur within the plant), may be precipitated in a stable form as aluminium hydroxide (gibbsite). According to Schofield, this precipitation takes place between pH 4 and 5, and the gibbsite remains stable at all higher values up to pH 9. On undergoing humification and mineralization, therefore, the snowgrass litter will release this gibbsite to the soil surface. The gibbsite will accumulate

in the topsoil (Tables 4 and 5) since even in the alpine humus soils pH values below 4 appear to be uncommon.

It might be noted from the foregoing that, contrary to the general impression in the literature, a vigorous earthworm population does not always require a nearly neutral soil. At least in the higher rainfall areas of New South Wales, a favourable combination of soil moisture and organic matter is more important than soil reaction. Under these conditions on the Monaro, earthworms have been observed in large numbers in soils as acid as pH 4·0. This difference is probably due to a difference in the requirements of the various species. There is a real need for further investigation into the identity and requirements of Australian earthworms and their role in soil formation.

In addition to the influence of snowgrass and earthworms, creep and solifluxion also contribute to the genesis of the alpine humus soils, since in sloping sites there is a continuous addition of rock and soil material from higher levels. The importance of the latter process can be seen from the well-developed stone line marking the average effective depth of solifluxion (frost-controlled soil creep). These processes probably also aid in the mixing of the mineral and organic fractions of the soil (cf. Plice, 1939). The small but regular additions of wind-blown dust referred to earlier may also contribute to the clay content of the topsoils.

The alpine humus soils are essentially soils in which the organo-mineral horizons dominate the profile. They are formed under climatic conditions in which acid organic matter has accumulated to such an extent that it dominates the physical and chemical properties of the soil almost to the exclusion of the effects of parent material and topography.

The high organic-matter content and the manner of its distribution through the soil is probably a factor preventing the development of podzolization, by combining with the polyvalent metals to form complex metallo-organic compounds in which the metals are not in the exchangeable form (Bremmer *et al.*, 1946).

Under these conditions of high soil moisture and strong acidity it would be expected that strongly podzolized soils would develop. That these are not formed is attributable in part to this stabilizing influence of the organic matter, and secondly to the circulation of fine soil material by the vigorous growth of snowgrass, earthworm activity, solifluxion, and soil creep.

Summary

A study has been made of the alpine humus soils of the Monaro region of New South Wales in relation to their environment and to associated soils. Their profile morphology, chemical characteristics, and clay mineralogy have been described.

Their profiles are best developed in the sub-alpine tract, where the combination of moisture and temperature appears to be optimum.

These soils are rich in organic matter, strongly acid in reaction, yet in spite of the high precipitations received, not only do they show no eluviation of sesquioxides or clay, but the clay content is actually at a maximum in the topsoil and falls gradually into the subsoil.

The organic matter is of mull type, penetrates deeply into the profile, and confers a stable crumb structure on the soil.

The exchange capacity is largely determined by the organic matter, and but slightly by the clay. The latter is largely clay biotite, with some kaolinite, and appreciable quantities of gibbsite, especially in the soils of the sub-alpine tract.

The topographic associates of these soils include bog peats, fen peats, silty bog soils, gley podzols, and under special conditions transitional alpine humus soils and brown podzolics.

Variation in the properties of the alpine humus soils may be correlated with altitude, as are also their relationships with other great soil groups. The altitudinal sequence studied included alpine humus soils, transitional alpine humus soils, brown podzolic soils, and iron podzols. The soil properties measured in this sequence included depth of weathering, horizon development, mechanical composition, organic matter, colour, H-ion concentration, and composition of the clay fraction. These have been related to the factors of the environment.

Acknowledgements

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REFERENCES

Braun-Blanquet, J. 1932. Plant Sociology. McGraw-Hill, New York and London.
Bremmer, J. M., Mann, P. J. G., Heintze, S. G., and Lees, H. 1946. Nature, **158,** No. 4022.
Chenery, E. M. 1951. J. Soil Sci. **2,** 95.
David, T. W. E. 1950. The Geology of the Commonwealth of Australia, vol. **1.** Arnold, London.
Deb, B. C. 1950. J. Soil Sci. **1,** 212.
Gibbs, H. S., Raeside, J. D., Dixon, J. K., and Merson, A. J. 1945. D.S.I.R. (N.Z.) Bull. No. 92.
Hallsworth, E. G., Costin, A. B., Gibbons, F. R., and Robertson, G. K. 1952. J. Soil Sci. **3,** 103.
Jenny, H. 1941. Factors of Soil Formation. McGraw-Hill, New York and London.
Joffe, J. S. 1936. Pedology. Rutgers, New Jersey.
MacEwan, D. C. 1946. J. Soc. Chem. Indust. **65,** 298.
Plice, M. J. 1939. Proc. Soil Sci. Soc. Amer. **4,** 346.
Prescott, J. A. 1931. C.S.I.R. (Aust.) Bull. No. 52.
—— 1944. C.S.I.R. (Aust.) Bull. No. 177.
Robinson, G. W. 1949. Soils, Their Origin, Constitution and Classification. Murby, London.
Russell, E. J. 1950. Soil Conditions and Plant Growth. Longmans, London.
Stephens, C. G. 1941. C.S.I.R. (Aust.) Bull. No. 139.
—— 1950. J. Soil Sci. **1,** 123.
Webb, D. A. 1947. J. Ecology, **35,** 105.
Zeuner, F. E. 1949. J. Soil Sci. **1,** 20.

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PLATE I

a. Subalpine tract, Kosciusko, showing sub-alpine woodland vegetation dominated by snow gum (*Eucalyptus niphophila*) on the slopes, and sod-tussock grassland vegetation dominated by snow grass (*Poa caespitosa*) along the valley. (Photo by W. R. Browne.)

b. The Kosciusko massif as seen in summer, showing the tree line of snow gum at the upper limit of the sub-alpine tract (foreground), and the alpine tract with melting snow patches and climatic climax vegetation of tall alpine herbfield (background). (Photo by W. R. Browne.)

c. The upper alpine tract near Mt. Kosciusko, showing tall alpine herbfields dominated by snow daisy (*Celmisia longifolia*) with snow grass. A glacial lake, Lake Cootapatamba, is shown in middle distance, and a semi-permanent snow patch on the higher ground at the right. (Photo by W. R. Browne.)

d. The alpine tract at Kosciusko as seen in midsummer, showing tall alpine herbfield vegetation of snow daisy (pale areas in left background) and snow grass (darker areas). A glacial cirque surrounded by well-developed lithosols is shown in right background. (Photo by F. V. Mercer.)

PLATE II

a. Profile of alpine humus soil in sub-alpine tract at Kosciusko, showing dense ground sward of snow grass, deep penetration of organic matter, rock floaters of gneissic granite, and worm-tracks in subsoil.

b. Profile of alpine humus soil in sub-alpine tract at Kosciusko, showing well-developed stone line (gneissic granite) due to solifluxion, and abundance of worm-tracks in subsoil.

c. Profile of shallow alpine humus soil developing on wet rock surface of gneissic granite in upper alpine tract near Mt. Kosciusko. Note dense sward of tall alpine herbfield vegetation dominated by snow daisy (pale foliage) and snow grass (darker foliage). A semi-permanent snow patch is shown in left background.

d. Profile of alpine humus soil developing from shallow humified peat and gneissic granite in upper alpine tract near Mt. Kosciusko. The vegetation is tall alpine herbfield dominated by snow daisy.

PLATE III

a. Profile of alpine humus soil formed on phyllite in alpine tract, Kosciusko. The vegetation is tall alpine herbfield dominated by snow grass.

b. Profile of alpine humus soil developing in association with silty bog soils in sub-alpine tract, Kosciusko, showing deep penetration of organic matter into the subsoil by means of worm-holes. The vegetation is a grassy heath dominated by shrubby species of *Epacris*.

b

d

a

c

A. B. COSTIN, E. G. HALLSWORTH, &c.—PLATE I

b

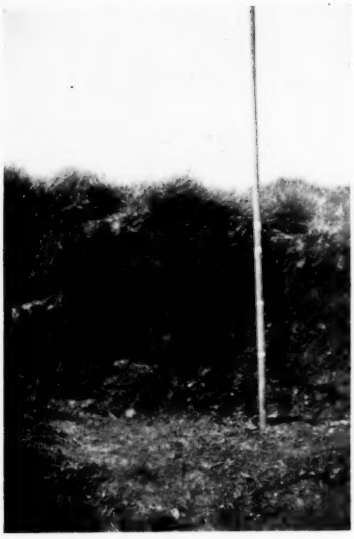
d

a

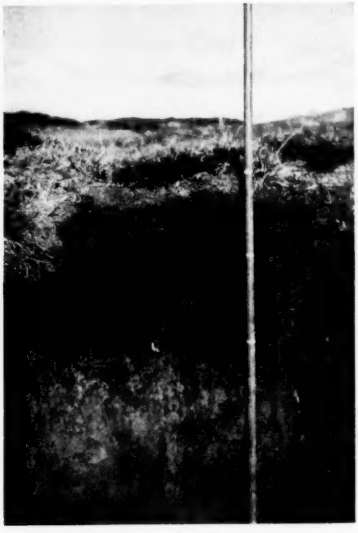
c

A. B. COSTIN, E. G. HALLSWORTH, &c.

PLATE II



a



b

A. B. COSTIN, E. G. HALLSWORTH, &c.

PLATE III

A STUDY OF ROCK WEATHERING WITH REFERENCE TO THE SOILS OF THE MALVERN HILLS

II. WEATHERING OF APPINITE AND 'IVY-SCAR ROCK'[1]

I. STEPHEN
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WITH ONE PLATE

I. *Introduction*

AN account of the mineralogical changes which occur during the formation of soil from two contrasted rock-types, granite and biotitite, of the Malvern crystalline-complex has been given in an earlier communication (Stephen, 1952). This paper presents a similar study of soil formation from representatives of the hornblendic rocks, and also summarizes the results regarding all the soils studied.

II. *Weathering of Appinite*

Profile description

Rocks rich in hornblende are abundantly represented in the Malvern crystalline-complex: in fact amphiboles are the outstanding minerals in most of the non-granitic rock-types. These rocks form part of a progressive evolutionary sequence, in which the earlier, more doleritoid, facies have been reconstituted to appinitic and ultimately hornblendite facies (Pocock, Brammall, and Croft, 1940).

Operations at Earnslaw Quarry have exposed a considerable area of the typical 'Earnslaw-type' appinitic facies, a hornblende-rich rock with pockets of white mica, albite, and quartz, a characteristic feature being the presence in the mica of inclusions of a carmine-tinted lamellar mineral. The margins of the pockets are rich in yellow epidote and grey-brown sphene.

The main mass of the appinite is traversed, in places, by veins of pure albite, more rarely by quartz veins, or by a combination of the two. Albite and quartz also occur as discrete 'knots' interspersed through the rock mass. The extent of these extraneous vein-materials was estimated at less than 5 per cent. at the site sampled.

In surface exposures the appinite develops a brownish rubbly weathering crust which is easily crumbled in the fingers. The coloration is due mainly to the accumulation of oxides and hydrous oxides of iron.

The description of the residual soil profile sampled is as follows:

Site: Earnslaw Quarry, the type-locality for the appinitic facies.
Vegetation: Grassland.
Depth:

0–1 in.	Dark reddish-brown humose loam, practically stoneless; porous and friable; matted with grass roots. pH 3·8.
1–6 in.	Dark brown sandy loam, small angular rock fragments less than 1 in. in diameter; porous, fine crumb structure; abundant roots. pH 4·0.

[1] Ivy-Scar is a local place-name.

6–15 in. Dark brown sandy loam very stony, angular rock fragments (appinite) up to 9 in. in length; porous, fine crumb structure; moderate number of fine roots. pH 4·3.

> 15 in. Shattered bedrock (appinite).

As in all the Malvern soils, a tendency to excessive drainage is shown by the dry fluffy nature of the soil.

Petrography of the unweathered facies

An analysis of the unweathered rock underlying the soil profile sampled gives the modal composition (average of seven microsections) shown in Table 1.

TABLE 1

Mode of Appinite

	%
Hornblende	60·2
Epidote-clinozoisite	16·3
Chlorite	7·5
Biotite	0·5
Hydromuscovite	6·8
Albite / Quartz	4·4
Sphene	2·1
Magnetite	2·0
Apatite	0·2

The dominant dark mineral is hornblende, which occurs in coarse grains and elongated prisms up to about 2 cm. in length: the smaller crystals show a marked tendency to euhedralism. Pleochroism is usually marked with X = light brown < Y = brownish-green < Z = blue-green, although the coloration is somewhat 'blotchy'. The extinction angle ($Z \wedge c$) is 25°, and the optic sign is negative. Finely disseminated iron ore, together with occasional epidote-clinozoisite, sphene, and chlorite, are frequently carried as inclusions in the crystals.

Chlorite occurs either as irregular masses showing no crystal outline, or, more commonly, as plates showing well-developed (001) cleavage, when pleochroism is marked from very pale yellowish-green to dark green. Varieties present include penninite, clinochlore, and prochlorite. The chlorite crystals are optically positive with negative elongation, and are usually sensibly uniaxial. Several of the plates show a residual core of hornblende, suggesting secondary derivation from the amphibole.

White mica (hydromuscovite) occurs in pockets as lath-shaped crystals up to 2 mm. in length: smaller crystals occur in decussate nests partly enclosed by hornblendes or larger chlorite crystals, and associated with albite, quartz, and the epidotic minerals. The presence of carmine-tinted intercalates[1] in the mica is a characteristic feature. Albite, normally in water-clear grains, and quartz of uneven distribution are habitual associates of the hydromuscovite. The margins of the pockets are rich in members of the epidote-clinozoisite group with variable amounts of sphene. Epidote occurs in two distinct forms: in granular aggregates associated with zoisite and clinozoisite and as larger crystals up to 2·5 mm.

[1] Possibly rhodochrosite or Mn-rich biotite.

in length. In thin section it shows neutral colours or slight pleochroic variation from pale grey-yellow to colourless.

Minerals present in minor amounts include iron ore, sphene, biotite, and apatite. Of these, sphene is the commonest, and occurs as brownish crystals normally with very ragged outlines. The iron ore is magnetite, in part titaniferous. Biotite may be entirely absent and never exceeds 4 per cent. in amount: when present it is always as an inclusion in hornblende. Its mode of occurrence suggests that it is a 'relic' of an antecedent more highly biotitic facies. It is usually channelled with prochlorite as a product of thermal hydrolysis.

Petrography of the weathering crust

An optical study of thin sections of the weathered crust of the appinite reveals two complementary trends of weathering of the ferromagnesian minerals leading to chloritic and vermiculitic products. Accompanying these changes is the separation of iron in the form of oxides and hydrous oxides.

Alteration of hornblende. Comparison of thin sections prepared from the fresh core-facies with those of the weathered crust developed on surface exposures indicates that the degradation of the hornblende can be represented by the following scheme:

Hornblende → chlorite + { excremental sphene and members of the epidote-clinozoisite group, haematite and brown iron oxides.
Hornblende → brown micaceous secondaries (allied to vermiculite).

Under the microscope it can be seen that the process of chloritization begins along edges and cleavage traces of the amphibole and gradually proceeds inwards along cracks. Patches and finely disseminated scales of greenish chlorite are developed within the amphibole crystals, which also show an irregular veining by green chlorite. In sections of the highly weathered rock hornblende remnants are enclosed in large areas of secondary chlorite (Plate I, B). This chlorite is feebly pleochroic in shades of light green, and occurs mainly in very fine matted aggregates, most of whose optical properties cannot be determined with certainty. Under crossed nicols it is practically isotropic or shows deep blue-grey polarization colours. Enclosed within the secondary chlorite are abundant small crystals of grey-brown sphene, colourless to yellow granules of weakly pleochroic epidote and clinozoisite, and irregular patches of haematite. It is noteworthy that haematite is entirely absent in the core-facies of the unweathered rock.

Geochemically the evolution of chlorite at the expense of hornblende in the early stages of weathering is important, as it involves the retention in the weathering crust of much of the magnesium liberated on the breakdown of the amphibole. It also appears probable that the calcium liberated is 'fixed' in secondary members of the epidote-clinozoisite group of minerals and sphene, by subsidiary reactions involving mainly (Ca, Al) and (Ca, Ti) respectively, since these are habitual associates of the

secondary chlorite. The mode of alteration observed is similar to that quoted by Van Hise (1904), who stated that 'hornblende under weathering conditions ordinarily changes to chlorite, which is often accompanied by epidote, calcite, quartz, iron oxides and siderite. . . . It is noticeable that the equation for the alteration of the hornblende to chlorite as a chief resultant product demands that epidote, calcite, siderite, quartz, and hematite be produced.'

The normal alteration of the hornblende in the early stages leads mainly to a chloritic product. Small amounts of brown mica are, however, directly formed by the breakdown of the hornblende. These are developed along cleavage traces as small flakes rarely exceeding 0·1 mm. in size, and their optical properties suggest their identity with vermiculite or a mixed-layer mica-vermiculite. It may be noted that the K_2O-content (0·64 per cent.)[1] of the hornblende is sufficient to explain the formation, at its expense, of small quantities of secondary minerals containing potassium as an essential constituent.

This mode of occurrence of secondary brown mica as an alteration product of hornblende is essentially the same as that described by Humbert and Marshall (1943) in a study of the weathering crust of diabase from Missouri, in which hornblende is converted to a micaceous mineral with biotitic optics. The hornblende was not considered primary but as due to the weathering of pyroxene. They state that 'secondary mica exists in light brown, strongly pleochroic flakes and scales—a constant companion of the secondary hornblende. The bluish green colors in the centers of the crystals of hornblende transform into turbid, weak yellowish green colors at the edges, reflecting an accumulation of small flakes of secondary mica. . . . The flakes of mica are isolated upon complete decomposition of the hornblende, and the position of large quantities in the lower horizons of the soil profile necessitates a relatively rapid transformation. The breakdown of the mica to the resultant clay minerals is an equally rapid process.'

Alteration of chlorite. The alteration of the plates of chlorite can be followed under the microscope by a progressive colour change from green to orange-brown and a reversal of the optic sign. The alteration generally begins at the edges of either 'books' of flakes or individual flakes, and along cleavage traces whence it gradually works inwards. The unweathered chlorite is green and optically positive, but the orange-brown material is optically negative. In particoloured flakes both optical characters appear, the green unaltered central portions of the flakes retaining their optically positive character, whilst marginally they are brownish in colour and optically negative. In some sections of the weathered appinite little of the original green chlorite is left, but is represented by optically negative pseudomorphs, which are pleochroic with X = very pale yellowish-brown $< Y = Z$ = brown. The acute bisectrix is nearly normal to (001) as in biotite, and the refractive indices, although showing slight variation, lie close to n_β ($= n_\gamma$) $1{\cdot}627 \pm 0{\cdot}005$, with birefringence moderate to strong.

[1] Dr. A. Brammall: personal communication.

A further feature is the concomitant development of small incipient crystallites of a translucent mineral, smoky-brown in colour, which can probably be referred to sphene. These crystallites are feathery in habit and tend to form small groupings in the brown altered areas while they are absent in the green unaltered portions of the flakes. Areas of chalcedonic silica (Plate I, c) occur in the weathered appinite and tend mainly to be associated with the altered chlorite where its separation between the cleavage planes is a marked feature.

Treatment of the brown micaceous flakes with cold hydrogen peroxide caused ready exfoliation suggesting their vermiculitic nature (Groves, 1939). X-ray analysis indicates their identity with a mixed-layer mica-vermiculite (common) and vermiculite (rare).

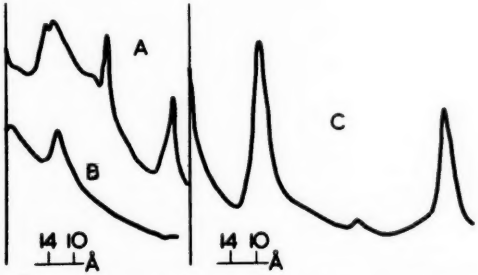


FIG. 1. *Alteration of chlorite.* Microphotometer tracings of X-ray diagrams of (A) slightly weathered chlorite flake, showing diffuse series of reflections of 24 Å period superimposed on the sharp 14 Å series of the original chlorite; (B) brown micaceous flake from weathered rock. Spacing 11·5 Å; (C) same flake, heated 540° C. Spacings 10, 5, 3·33 Å.

The presence of a mixed-layer mica-vermiculite is shown by interplanar spacings, normal to (001), between 10 and 14 Å (Fig. 1, B), which condense to give a mica structure (10, 5, 3·33 Å) when heated at 540° C. (Fig. 1, C). Assuming, as Gruner (1934) has done, that the intermediate spacings are the result of interstratification of 10 Å (non-hydrated) and 14 Å (fully hydrated) units, the material in the early stages of weathering tends towards a metastable phase in which these units are present in approximately equal amounts, as the majority of the flakes show a strong basal reflection in the region of 12 Å, when a 24 Å reflection is usually seen, being due to the sum of the 10 and 14 Å units. Fig. 1, A illustrates this trend of alteration and shows a rather diffuse series of reflections having spacings of 24 Å/*n*[1] superimposed on the sharp series of 14 Å/*n* reflections of the original chlorite. On further weathering, the chlorite diagram is eliminated leaving a series of hydrated trioctahedral mica reflections characteristic of the brown micaceous flakes occurring in both the highly weathered rock and the overlying soil.

It is not necessary to postulate a complete breakdown of the chlorite

[1] The symbol */n* indicates a sequence of higher order.

crystals on weathering. The secondary mixed-layer mica-vermiculite (or vermiculite) shows a marked preferential orientation on X-ray diagrams corresponding to that of the original chlorite. The change may, therefore, be attributed to atomic rearrangement within the crystals with introduction of potassium.

Alteration of other minerals. The other minerals are much more stable than the hornblende and chlorite and are essentially unaltered in the weathered rock.

Epidote, zoisite, and clinozoisite appear relatively resistant, except for a slight fracturing in the larger grains and the deposition of minor quantities of brown iron oxide along the fracture planes.

The albite which occurs in close association with the hydromuscovite becomes clouded and suffers alteration to a generally low-refracting aggregate. The condition of the albite compared with that of the hydromuscovite is a good test of the freshness of the specimen, as in the fresh rock it is extremely difficult to discriminate between these species.

Petrography of the soil

Sand fractions. The most marked change in the character of the mineral suites in passing from bedrock into the overlying soil appears in the micaceous minerals of the trioctahedral group. In the sand fractions of the soil more than 85 per cent. of these minerals consist of brown micaceous flakes of vermiculitic nature with a golden or bronzy lustre, whereas in the fresh core-facies of the parent appinite they are absent and the dominant trioctahedral mineral is green chlorite of hydrothermal origin. This is illustrated for the fine sands in Table 2, which shows the distribution of the 'light minerals' in the layers of the profile.

TABLE 2

Distribution of 'Light Minerals' (s.g. < 2·90) in the Fine Sand (0·2–0·02 mm.) Separates of Soil overlying Appinite

Depth	0–1 in.		1–6 in.		6–15 in.	
Minerals	%		%		%	
Brown micaceous flakes (vermiculitic)	10·7	11·6	12·6	14·5	20·6	23·3
Green micaceous flakes (chlorite)	0·3		0·6		1·5	
Particoloured flakes	0·6		1·3		1·2	
Hydromuscovite	4·4		4·1		5·1	
Albite	28·4		32·8		31·9	
Quartz	50·5		42·0		36·4	
Chalcedony	2·2		4·4		2·1	
'Coated grains'	2·9		2·2		1·2	

Note: Percentages are based on microscopic counts of approximately 300 grains in about 20 random fields for each sample.

In the sands the chlorite occurs as green flakes of an optically positive character, corresponding to the chlorite of the unweathered bedrock. The very small amount remaining illustrates its ready susceptibility to alteration. In thin sections of the weathered rock, chlorite is one of the first minerals to show signs of weathering, and its alteration to a brown

micaceous pseudomorph has already been described. The latter is in brown to orange-brown flakes yielding good interference figures with $(-)2V 8-10°$. The majority of the flakes from the bottom layer of the profile, on X-ray analysis, show a basal spacing at 11·5–12 Å such as occurs in hydrobiotite, the mixed-layer mineral described by Gruner (1934) as consisting of approximately equal amounts of mica and vermiculite layers. In the upper more highly weathered layers progressive alteration towards a 14 Å product (vermiculite) occurs.

The flakes of white mica can be identified with the hydromuscovite of the parent appinite by their characteristic carmine-tinted inclusions. The small amount in all layers of the profile shows their limited stability to physical weathering.

The occurrence of comparatively large amounts of albite and quartz in the sand fractions can be attributed to the presence of veins of these minerals cutting the main body of the appinite, and their concentration relative to the ferromagnesian minerals in the coarser grades of the soil is due to their resistance to physical and chemical weathering. Chalcedony, characterized by its low refractive index and low birefringence, is also present and shows little variation in amount throughout the profile.

The 'heavy separate' (s.g. $>$ 2·90) of the fine sands approximates to 40 per cent. by weight in all the layers of the profile, hornblende and members of the epidote-clinozoisite group being the dominant minerals. In the basal layer the epidote: hornblende ratio is approximately 0·5 : 1, but in the surface soil it has increased to 0·8 : 1. This increase does not appear to be due to any appreciable formation of epidotic minerals in the soil, but to their relative stability compared with the hornblende.

Of the remaining minerals sphene, iron ore, and zircon are the commonest. The sphene occurs as brownish, irregularly shaped grains, often fractured. The iron minerals are haematite in anhedral grains and magnetite in octahedral or (more commonly) rather rounded grains. Partial alteration of the latter mineral to haematite and ilmenite is common.

Zircon occurs rarely as perfect euhedra showing pyramidal terminations, but is usually subangular to rounded or squat and slightly rounded. The grains are colourless or have a faint purplish tinge. Garnet (almandine) is rare, but was observed in all layers of the profile. These species are present in minor amounts in the appinite, and are relatively concentrated in the overlying soil owing to their high resistance to weathering.

Clay mineralogy. The X-ray diagram given by an oriented aggregate of the soil clay ($< 0·5\ \mu$) separated from the bottom layer of the profile, and illustrated in Fig. 2 A, shows a series of (00*l*) reflections of 14 Å and submultiples, and a weaker series of 10 Å and submultiples (marked I).

The general pattern of the reflections and the response to heat-treatment is the same in the clays from all the layers of the profile, and within different size-separates of the same clay. The relative intensities of the lines, however, show minor variations from sample to sample, reflecting a variation in the amounts of the different components present. There is no change in the position of the lines on treating the clay with glycerol, indicating the absence of both montmorillonite (MacEwan, 1944) and 'swelling chlorite' (Stephen and MacEwan, 1950).

After heat-treatment at 540° C. (Fig. 2, B) a well-marked composite structure develops on the low-spacing side of the 14 Å line. This structure has been analysed in the way previously described (Stephen, 1952) and reveals the presence of three symmetrical peaks with spacings of 13·8, 11·8, and 10 Å in all the clays (Fig. 2, C).

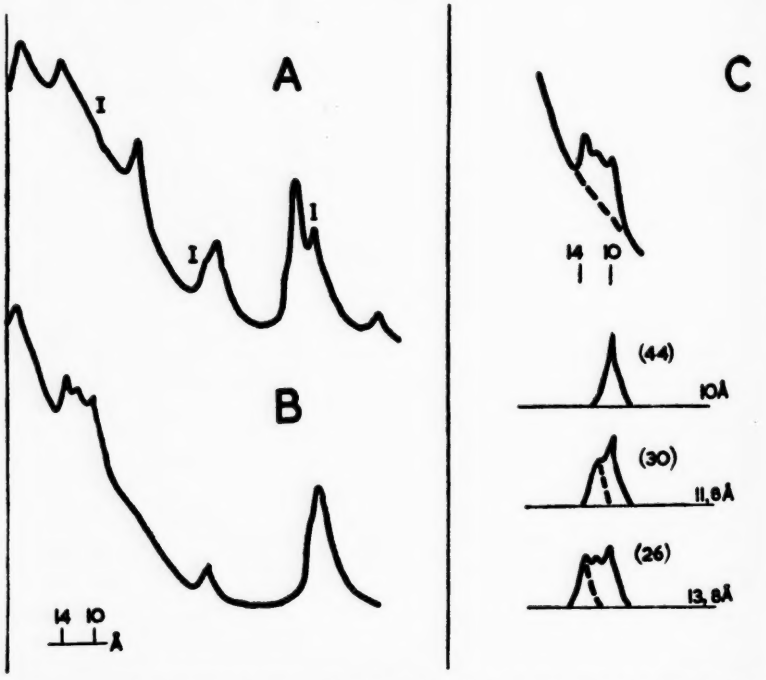


FIG. 2. Microphotometer tracings of X-ray diagrams of the clay (< 0·5 μ) from the basal layer of the profile (A) before and (B) after heating at 540° C.: (C) shows the analysis of the peaks in the 10–14 Å region of the heated clay. Figures in brackets give the areas of the individual peaks as a percentage of the total area of the curve.

The data indicate that there are four crystalline phases present:

(*a*) a chloritic phase, giving a 13·8 Å reflection on heating;
(*b*) a vermiculitic phase, giving a 10 Å reflection on heating;
(*c*) a random mixture of (*a*) and (*b*) in approximately equal amounts; and (*d*) an illitic phase giving a 10 Å reflection on the unheated clays.

Phases (*a*), (*b*), and (*c*) appear to form one system (trioctahedral), as in the clays developed on biotitite, while the mica lines on the photographs of the unheated clays agree best with the assumption that a muscovite-like (dioctahedral) mineral is present.

It has not been possible to reach a definite conclusion as to the type of chlorite present. The modifications in the intensities of the basal reflections on heating penninite and other magnesian chlorites have been

studied by Brindley and Ali (1950). They found that when penninite was heated at 600° C. marked changes occurred, the (001) reflection becoming many times more intense, while the (002), (003), and (004) were considerably weakened. The general distribution of the lines, however, remained essentially the same, and the structure was still that of a chlorite. At 760° C. the material was largely broken down and gave a very diffuse pattern corresponding to the stronger penninite lines.

The chlorite in the soil clays shows similar thermal effects but at lower temperatures. At 540° C. the higher order chlorite lines disappear, but a sharp (001) reflection remains, probably with enhanced intensity. After heating at 750° C. for several hours the lines of the chlorite pattern are eliminated. The general distribution of the chlorite lines on a powder photograph shows a marked resemblance to that of penninite, but with fewer lines, as in the clays overlying biotitite. This observation and the fact that the thermal effects occur at lower temperatures suggest that the chlorite is probably allied to penninite, though less well crystallized.

The vermiculitic component appears identical with that occurring in the soil clays overlying biotitite, and occurs both as a separate entity and as a mixed structure with chlorite. The presence of an illitic mineral is shown by the sequence of 10 Å reflections on the unheated clays, and the intensities agree with those expected from a mineral of the muscovite-crystallization. It has already been shown that this component is absent from the clays overlying biotitite, but is the dominant clay material in the soils of the granitic area (Stephen, 1952).

Estimated amounts of components. Although a sample of clay from the crust of the weathered appinite contains small amounts of a material having a limited *c*-axis expansion on treatment with glycerol (Stephen and MacEwan, 1951), when heated at 540° C. it shows three peaks (13·8, 11·75, and 10·05 Å) in positions almost identical with those of the soil clays, although the relative intensities of the lines are markedly different.

On the basis that the 11·8 Å phase represents a random mixture of the 13·8 Å (chloritic) and 10 Å (mica-like) phases in approximately equal amounts, the proportions of these components in samples of the clay from the weathered rock and the soil have been determined, and percentages are given to the nearest 5 per cent. in Table 3. A subdivision of the 10 Å phase has been made on the basis of the relative intensities of the first three lines of the (00*l*) series, assuming

(*a*) the second-order basal reflection at 5 Å is zero or very weak in the 'collapsed vermiculite' structure (cf. Fig. 1, c);

(*b*) the relative intensities of the (00*l*) lines of the dioctahedral illite are comparable with those of the hydromuscovite of the parent rock.

The figures in Table 3 have no *absolute* value, as the intrinsic intensities of the lines are not known, but for comparisons of *relative* amounts they are consistent, and three main points emerge:

1. There is a significant increase in the proportion of vermiculite layers relative to chlorite layers in passing from the weathered rock into the overlying soil.

2. In different size-separates of the same sample the proportion of vermiculite layers relative to chlorite layers increases with decrease in particle-size: this is particularly marked in the weathered rock.
3. In the different layers of the soil profile there is no significant differentiation in amount of the mineral components.

Observations 1 and 2 suggest the weathering of a chloritic towards a vermiculitic product in the clays, consistent with the conclusions drawn from the biotitite soil.

TABLE 3

Calculated Proportions of Chloritic and Mica-like Layers as determined by Heating at 540° C., and applying Theory of Diffraction by Randomly-mixed Layers

Size-grade	$< 2\mu$			$< 0{\cdot}5\mu$		
	% 14 Å *phase*	% 10 Å *phase*		% 14 Å *phase*	% 10 Å *phase*	
	Chlorite	*Vermiculite*	*Illite*	*Chlorite*	*Vermiculite*	*Illite*
Clay from soil (0–1 in.)	45	30	25	n.d.	n.d.	
Clay from soil (1–6 in.)	50	30	20	n.d.	n.d.	
Clay from soil (6–15 in.)	45	30	25	40	35	25
Clay from weathered rock	75	15	10	55	35	10

The relative amounts of the trioctahedral and dioctahedral components given in Table 3 are in good agreement with the estimates made from the relative intensities of the two distinctive (060) lines on the powder diagrams (MacEwan, 1949). On the diagrams of the soil clays two lines in this region are well marked, a strong line at 1·526 Å (trioctahedral region) and a weaker line at 1·494 Å (dioctahedral region). An estimate of the 'triocta: diocta' ratio on the basis of the relative intensities is of the order of 4 or 5:1, indicating that the amount of dioctahedral component in the clays approximates to 20 per cent. The dioctahedral constituent appears to be exclusively illitic, although the occurrence of a few per cent. of kaolin cannot be entirely excluded.

Summary

It has been shown that in the soils derived from appinite, minerals of the chlorite-vermiculite crystallization form the dominant part of the clays. Optical study of thin sections of the weathered rock shows that the clay is mainly derived from the breakdown of the hornblende, which on weathering initially yields mainly chloritic products. The finely crystalline nature of this secondary chlorite is shown by the fact that it forms the dominant constituent of the $< 2\mu$ fraction of the weathered rock and is a prominent component of the clays of the overlying soil, but is virtually absent in the sand fractions. Further weathering proceeds to

vermiculitic products through mixed-layer chlorite-vermiculite intermediate stages.

It is probable that the subsidiary illite in the clays is mainly derived from the breakdown of the hydromuscovite of the parent rock, as the comparative scarcity of this mineral in the coarser fractions of the soil shows its limited resistance to physical weathering. An alternative mode of origin is as a decomposition product of the feldspar.

III. *Weathering of 'Ivy-Scar Rock'*

Profile description

The 'Ivy-Scar rock' is essentially a granophyric quartz micro-diorite and has a widespread distribution in the Malvern Hills. An excellent locality for its homogeneity is the Worcestershire Beacon expanse, which provides an almost uniform area for soil profile work: the whole of the slope up to the crest is 'Ivy-Scar' and there is no risk of contamination with other material.

The description of the residual soil profile sampled is as follows:

Site: 100 yds. north of Indicator on Worcestershire Beacon, gentle slope on west side of top of ridge.
Vegetation: Patches of short grass, bedstraw, and mosses.
Depth:
0–1 in. Dark grey humose loam. pH 3·8.
1–12 in. Warm brown fine sandy loam, fluffy, full of angular rock-fragments; fine fibrous roots abundant to base. pH 4·0.
> 12 in. Passing into bedrock.

It is characteristic of 'Ivy-Scar' that the vegetation is very poor and sharply marked off from the thick bracken growing on granite. Most of the soil is very thin indeed with bare rubble exposed. At the crest of the hill the thin soil has been washed away, exposing bare rock, and at a lower level on the slope humose granules are entrapped in grass. The samples were taken from a deeper soil than the average.

Petrography

The rock consists of green hornblende and plagioclase feldspar, with subsidiary micropegmatite, iron oxides, and apatite. Epidote, chlorite, and sphene are present as secondary minerals. To apparently similar rocks with plagioclase phenocrysts and micropegmatitic groundmass, Hatch (1909) gave the name markfieldite from their occurrence at Markfield in the Charnwood Forest, Leicestershire.

A mineral analysis of the essentially unweathered rock underlying the soil profile sampled gives the composition (average of 5 microsections) shown in Table 4.

The dominant feldspar is a sodic plagioclase (oligoclase or oligoclase-andesine), which occurs in well-formed lath-shaped crystals. A zonal alteration of the feldspar to a product giving a generally low-refracting aggregate-reaction to polarized light is common, the central portions of the crystals being the most highly altered. This alteration, being present in apparently fresh specimens of the rock, may best be attributed to hydrothermal action. In the weathered rock, alteration of the feldspar has

produced significant amounts of sericitic white mica giving in aggregate a confused reaction to polarized light and exhibiting high interference colours.

TABLE 4

Mode of 'Ivy-Scar Rock'

	%
Hornblende	22·0
Feldspar	48·0
Quartz	9·0
Epidote-clinozoisite	2·5
Chlorite	7·8
Iron ore	10·2
Sphene	<0·5
Apatite	<0·5

The hornblende is a pale green fibrous variety, weakly pleochroic. Its stability to weathering is limited and its decomposition products, as in the appinite, are mainly chlorite, members of the epidote-clinozoisite group of minerals, sphene and brown (mainly amorphous) iron oxides.

Quartz occurs mainly in intergrowths as interstitial micropegmatite, but some separate small anhedral crystals are present. The presence of skeletal crystals of ilmenite altering to leucoxene is a marked feature of this rock. Apatite is a common accessory.

Petrography of the soil

Sand fractions. The amounts and distribution of the minerals in the fine sand separates are shown in Table 5.

TABLE 5

Distribution of Minerals in the Fine Sand (0·2–0·02 mm.) Separates of the Soil overlying 'Ivy-Scar Rock'

Depth	1–5 in.	5–9 in.	12–15 in.
'Light minerals' (s.g. <2·90)			
Quartz	49·6	43·3	37·4
Feldspar / Micropegmatite	44·3	49·6	48·2
Brown micaceous flakes (vermiculitic)	1·4	1·8	2·5
Chlorite	0·6	1·5	5·5
White mica ('sericite')	1·9	2·4	4·9
'Coated grains'	2·2	1·5	1·5
'Heavy minerals' (s.g. >2·90)			
Wt. % heavy minerals	*8*	*6*	*5·5*
Hornblende	28·9	37·1	41·0
Epidote, zoisite, and clinozoisite	28·0	29·0	27·3
Iron ore	32·9	25·2	23·7
Sphene	2·3	2·9	2·4
Zircon	2·9	1·0	1·2
Garnet	1·4	1·6	0·9
Tourmaline	0·9	1·3	0·9
Apatite	..	..	1·2
'Coated grains'	2·6	1·9	1·5

Note: Percentages are based on microscopic counts of approximately 300 grains in about 20 random fields for each sample.

The most striking feature is the low percentage of heavy minerals in the soil compared with the amount (*c.* 40 per cent.) in the parent rock. This emphasizes the ease of weathering of the ferromagnesian minerals compared with the quartz and feldspar that form the bulk of the sand fractions.

Comparing the distribution of the minerals with the composition of the parent rock, it can be seen that weathering has caused very significant reductions in the amounts of hornblende, and, to a lesser degree, of the epidotic minerals, and it is reasonable to assume that, when accession of new material from rock fragments in the profile ceases (a stage not yet reached), these minerals will be eliminated from the weathering system under the low pH prevailing. In the fresh parent rock epidote-clinozoisite occurs only in small amount, but is more abundant in the weathered rock as one of the products of the breakdown of the hornblende, and this progressive increase relative to the hornblende can be followed in passing up the profile, but the absence of any marked accumulation in the upper layers points to its limited stability.

Iron oxides are abundant in the heavy separates in all layers of the profile, and the slight increase in the amounts of the heavy separate in the surface soil is due to a relative accumulation of crystalline iron oxides and iron-coated minerals. A marked feature during the weathering of the rock is the alteration of the magnetite (and more rarely ilmenite) to haematite. Haematite is absent in the unweathered core-facies but is present in samples of the highly weathered rock and is conspicuous, though subsidiary to magnetite and ilmenite, in the soil.

Apart from brownish sphene, zircon is the commonest of the accessory minerals. Perfect euhedral crystals, normally colourless or with a faint purplish tinge, are common, and are often strongly zoned and contain numerous inclusions. Tourmaline is present in small crystals of prismatic habit, strongly pleochroic in shades of brown. The coffee-brown variety is the commonest, but light yellowish-brown, violet-brown, and a greenish-brown variety with many inclusions were also noted. Garnet occurs in both colourless and slightly pinkish varieties, the grains being normally angular to subangular.

The light minerals present no feature of particular interest, the bulk of the separate being composed of quartz and feldspar. The latter mineral shows aggregate polarization effects under crossed nicols, due to the development of decomposition products, and is frequently coated with brownish iron oxide. Chlorite is common in the basal layer of the profile but is scarce in the upper layers and, apart from the white mica liberated on the breakdown of the feldspar, the main micaceous constituent of the upper layers is a brown mica of the mixed-layer mica-vermiculite type.

Clay mineralogy. The diffraction pattern given by oriented aggregates of the clays (Fig. 3, A) shows two integral series of basal reflections, one of 14 Å (chlorite-vermiculite) and the other of 10 Å (illite) period. The first two orders of the kaolin basal reflections are superimposed on the second- and fourth-order basal lines of the chlorite-vermiculite series. Lines due to quartz are also present, the strong reflection at about 3·35 Å

being superimposed on the third-order basal illite reflection at 3·33 Å, while a further quartz line (4·2 Å) can be observed on the tracing between the second- and third-order illite basal reflections.

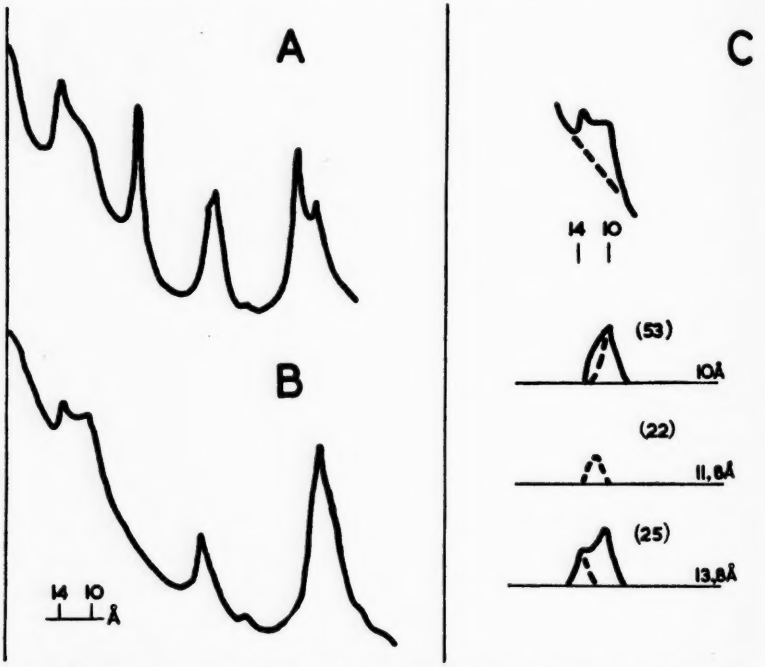


FIG. 3. Microphotometer tracings of X-ray diagrams of the clay (< 2μ) from the 5–9 in. layer of the profile (A) before and (B) after heating at 540° C.: (C) shows the analysis of the peaks in the 10–14 Å region of the heated clay. Figures in brackets give the areas of the individual peaks as a percentage of the total area of the curve.

After heat treatment at 540° C. two sharp lines at 14 and 10 Å remain, the latter with a well-defined series of higher orders (Fig. 3, B) indicating minerals of the chlorite and illite groups respectively. The structure in this region has been analysed (Fig. 3, C), after the curves were replotted on a horizontal base-line, on the basis that the inner (high-spacing) edge and the outer (low-spacing) edge of the 14 and 10 Å lines, respectively, represent their true shape and that the peaks are symmetrical. After subtracting the two peaks thus obtained from the total area of the curves a small symmetrical residue of spacing 11·8 Å remains. This structure appears analogous to that developed with similar spacing in the clays overlying biotitite and appinite, where it has been interpreted as due to a random mixture of chloritic and vermiculitic phases in approximately equal amounts.

The illite pattern, in the heat-treated clay, is dominantly of the dioctahedral type, as shown by the relative intensities of the second- and

third-order basal lines, after allowance has been made for the superposition of the strong quartz reflection on the latter. The presence of small amounts of a 'collapsed vermiculite' component is shown, however, by the change in relative intensities of the 10 and 14 Å lines before and after heat-treatment of the clay.

Apart from quartz, which is markedly concentrated in the coarse clay, the components show little variation in amount within different size-separates, or in the different layers of the profile, and the estimated composition of the clays falls within the following range expressed as percentages: dioctahedral illite 35–45, chlorite 30–35, vermiculite 15–20, kaolin 5–10, quartz < 5.

On the powder diagrams the approximately equal intensities of the two distinctive (060) lines show that the trioctahedral and dioctahedral components occur in approximately equal amounts consistent with the estimated compositions.

Summary

It has been established that in the soil clays overlying the 'Ivy-Scar rock' trioctahedral and dioctahedral minerals are present in approximately equal amounts. The components are the same as those developed in the other soil clays studied, the trioctahedral member being a chlorite-vermiculite crystallization, and the dioctahedral constituents illite and kaolin. In addition, small quantities of quartz are present.

The presence of these minerals can be directly related to the mineralogical composition of the parent rock, and to the trend of alteration of the primary minerals as seen in sections of the weathered rock. In such sections the decomposition of hornblende to finely-crystalline secondary chlorite is well seen, and the subsequent alteration to vermiculite is attributable to further weathering in the soil. The origin of the illite appears to be entirely due to the alteration of the feldspar, fine-grained white mica being abundantly developed at its expense in the weathered rock.

That the hornblende is a more active 'clay-former' than the feldspar is shown by the approximately 1 : 1 ratio of chlorite-vermiculite to illite+kaolin in the clays, although the hornblende : feldspar ratio in the parent rock is approximately 1 : 2. Confirmatory evidence that the hornblende is less stable than the associated feldspar is afforded by the small amount of hornblende relative to feldspar remaining in the sand fractions of the soil.

IV. *General Discussion*

This study is a comparison of the products of weathering from four crystalline rocks of different mineralogical composition, the soil-forming factors, climate, topography, vegetation, and time being the same. Under these conditions the profiles investigated show strikingly the effect of the parent bedrock in determining the mineralogical composition of the derived soils.

Fig. 4 shows schematically the average composition of the clay fractions of each of the soils and the variation with the rock-types studied. The modal percentage of the dark minerals (dominantly ferromagnesian

silicates, but excluding muscovite) have been plotted horizontally. The estimated proportions of the components of the clay fractions of the derived soils have been plotted vertically. The histogram also shows the average amount of 'free' sesquioxides extracted from the clays, using acid ammonium oxalate (Tamm, 1934).

The derived soils from the ultra-basic rocks contain clay minerals of the chlorite-vermiculite crystallization, while those from the granite con-

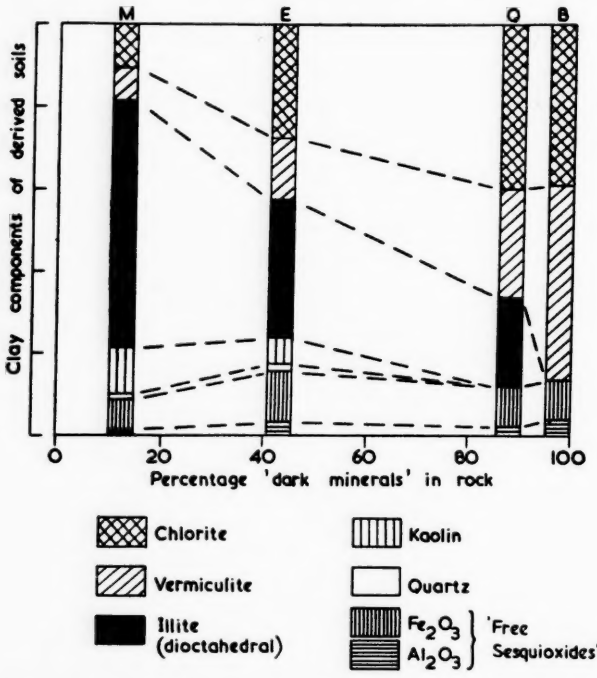


FIG. 4. Variation in the constitution of the clays of the derived soils with difference in parent bedrock. M = granite; E = 'Ivy-Scar rock'; Q = appinite; B = biotitite.

tain mainly illite. Both types of clay minerals are prominent constituents of the soil colloids formed from the 'Ivy-Scar rock'. Apart from these minerals the other crystalline constituents of the soil clays are kaolin and quartz, associated with the more acid rocks.

Origin of chlorite-vermiculite. A comparison of the decomposition products of the biotitite with those of the appinite reveals a close similarity in the trend of weathering. The finer fractions of the soil overlying biotitite consist almost exclusively of chlorite-vermiculite, and in the soil overlying appinite it forms the dominant part of the clays. In both cases the conditioning factor is the early formation of chlorite in the weather-

ing system, at the expense of initial biotite in the biotitite and of the hornblende in the appinite, and its subsequent alteration to vermiculite.

It is of interest to consider how this change from chlorite to vermiculite may take place. The formula of the original chlorite may be represented by

$$\underset{\text{Mica-layer}}{[Si_6Al_2]^{IV}[Mg_6]^{VI}O_{20}(OH)_4} + \underset{\text{Brucite-layer}}{[Mg_4Al_2]^{VI}(OH)_{12}}$$

although actually it will be more complicated due to the presence of ferrous and ferric iron. Weathering in the soils is taking place at a fairly low general pH (<5), i.e. there is a considerable concentration of hydrogen ions. These may penetrate into the brucite layer and remove Mg^{2+} ions by an exchange process, the ultimate effect being that the H^+ may add on to $(OH)^-$ groups forming H_2O molecules. The net effect would be to convert two $(OH)^-$ groups into neutral water molecules for each Mg^{2+} ion removed, leaving the charge on the layer unchanged. The process could go through such stages as

$$Mg_3Al_2(OH)_{10}\,(H_2O)_2$$

until the residue is $Al_2(OH)_4(H_2O)_8$,

all the Mg^{2+} have been removed. The structure of the brucitic layer has remained exactly the same, certain of the $(OH)^-$ groups have been replaced by H_2O molecules (having the same size), and most of the octahedrally co-ordinated positions have become vacant. When the last stage is reached, however, the residue consists of isolated $Al(OH)_2^+$ groups, linked with water molecules only, i.e. the brucitic layer has been completely disintegrated, and an aluminium vermiculite remains, in which the Al^{3+} ions should be mobile and exchangeable. It has been assumed that all the Mg^{2+} ions will be removed leaving the Al^{3+} ions intact. Actually it seems likely that the Al^{3+} ions will also be attacked to some extent, so that the result will be an Al–Mg vermiculite. When formed, this may of course attract other ions by cation exchange.

These considerations suggest that a complete range of intermediate minerals between chlorite and vermiculite is possible, and this is compatible with the observations. Should the pH be raised, the reverse process may be postulated, consisting of a transfer of H^+ ions from the mineral to the solution and the taking up of Mg^{2+} or other ions from the solution.

Origin of illite. Two modes of origin of the illite in the soil clays are indicated. The illite in the soil clays overlying granite and the 'Ivy-Scar rock' is demonstrably due to the alteration (probably in part hydrothermal) of the feldspar of the bedrock, and it is probable that in the soil clays overlying appinite the subsidiary illite is mainly derived from the breakdown of the hydromuscovite in the parent rock.

It should be noted that illites are the only clay minerals that contain non-exchangeable potassium as an essential constituent, and in this respect they are intermediate between potash feldspar of the primary

crystalline rocks and kaolin and montmorillonite of the sedimentary rocks. This suggests that illite may be typical clay mineral in sediments representing early stages in the weathering of rocks of granitic composition. Support for this view is obtainable from field evidence. In accounts of the mineralogy of soil clays developed from rocks of granitic character (Kelley, Dore, *et al.*, 1938, 1939) the common occurrence of the illite-kaolin association is noteworthy, and the evidence suggests the existence of the evolutionary trend,

$$\text{(feldspar)} \longrightarrow \text{illite} \longrightarrow \text{kaolin},$$

the reaction occurring under acid leaching conditions. Under alkaline conditions the weathering of illite to a montmorillonitic product would be anticipated.

The conclusion to be deduced from the occurrence of large amounts of chlorite and illite in the clays is that the soils represent an early stage in the weathering sequence. This is supported by the presence of comparatively large amounts of unweathered (though readily weatherable) minerals in the sand fractions.

Summary

A study of four residual soils derived from different members of the Malvern crystalline-complex has shown the importance of the bedrock in determining their mineralogical composition. The coarser material in the soils consists mainly of the relatively unweathered minerals characteristic of the underlying rock, whilst the composition of the colloidal material reflects the trend of alteration of the primary minerals on weathering. The colloids of the soils derived from the ultra-basic biotite- and hornblende-rich rocks consist mainly of chlorite-vermiculite. With increase in the feldspar content of the bedrock (diorite), dioctahedral illite in addition becomes prominent in the soil colloids, and is dominant in those derived from granite.

REFERENCES

BRINDLEY, G. W., and ALI, S. Z. 1950. X-ray study of thermal transformations in some magnesian chlorite minerals. Acta Cryst. **3**, 25–30.

GROVES, R. 1939. Exfoliation of vermiculite by chemical means. Nature, **144**, 554.

GRUNER, J. W. 1934. The structure of vermiculites and their collapse by dehydration. Amer. Miner. **19**, 557–75.

HATCH, F. H. 1909. Text-book of Petrology. 5th ed., London.

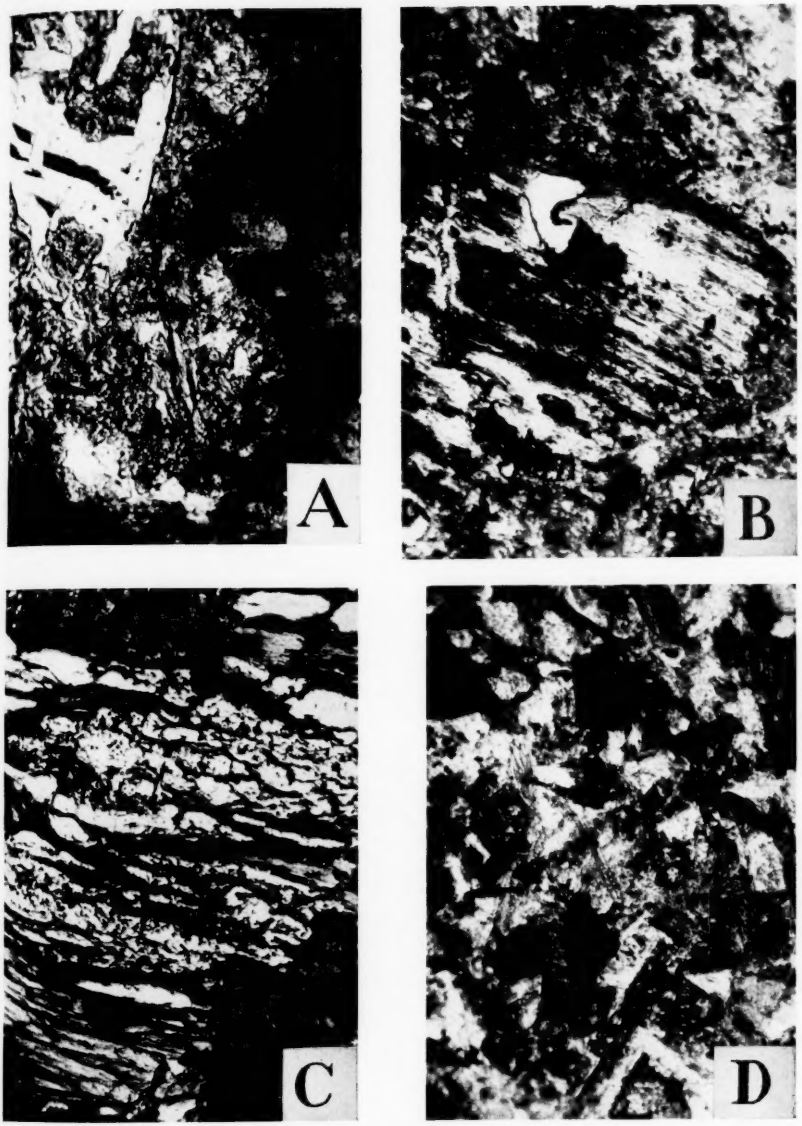
HUMBERT, R. P., and MARSHALL, C. E. 1943. Mineralogical and chemical studies of soil formation from acid and basic igneous rocks in Missouri. Miss. Agric. Expt. Sta. Res. Bull. **359**.

KELLEY, W. P., and DORE, W. H. 1938. The clay minerals of Californian soils. Proc. Soil Sci. Soc. Amer. **2**, 115–20.

—— —— WOODFORD, A. O., and BROWN, S. M. 1939. The colloidal constituents of Californian soils. Soil Sci. **48**, 201–55.

MACEWAN, D. M. C. 1944. Identification of the montmorillonite group of minerals by X-rays. Nature, **154**, 577–8.

—— 1949. Some notes on the recording and interpretation of X-ray diagrams of soil clays. J. Soil Sci. **1**, 90–103.



A. *Appinite.* White mica with characteristic lamellar inclusions, surrounded by minerals of the epidote-clinozoisite group, with hornblende on right of field. Ordinary light, × 50.

B. *Weathered appinite.* Weathering hornblende phenocryst enclosed in area of secondary finely granular chloride. Ordinary light, × 50.

C. *Weathered appinite.* Separation of secondary chalcedonic silica (white areas) in association with altered chlorite. Ordinary light, × 50.

D. *'Ivy-Scar rock'.* Lath-shaped plagioclases, hornblende, iron ore, with fine-grained micropegmatitic groundmass. Ordinary light, × 50.

Photomicrographs by V. Stansfield, F.R.P.S.

I. STEPHEN—PLATE I

POCOCK, R. W., BRAMMALL, A., and CROFT, W. N. 1940. Easter field meeting, Hereford. Proc. Geol. Assoc. **51,** 52–62.

STEPHEN, I. 1952. A study of rock weathering with reference to the soils of the Malvern Hills. Part I. Weathering of biotitite and granite. J. Soil Sci. **3,** 20–33.

—— and MACEWAN, D. M. C. 1950. 'Swelling chlorite'. Géotechnique, **2,** 82–83.

—— —— 1951. Some chloritic clay minerals of unusual type. Clay Miner. Bull. **1,** No. 5, 157–62.

TAMM, O. 1934. The oxalate method of soil analysis. Medd. Skogsförsöksanst, **27,** 1–20.

VAN HISE, C. R. 1904. A treatise of metamorphism. Monogr. XLVII, U.S. Geol. Surv. Washington.

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THE PHYSICO-CHEMICAL BEHAVIOUR OF NUTRIENTS IN SOILS

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IONIC nutrients in soils may occur purely as exchangeable ions, or they may be present in more or less crystalline, well-defined compounds as well. Depending on this and on the properties of the individual nutrient, the equilibrium concentration in the soil solution is governed by various physico-chemical factors, such as pH, dissociation constants, solubility products, and oxidation-reduction potentials. From such data the qualitative behaviour and, in some cases, the order of magnitude of the equilibrium concentration under different conditions can be estimated. The main purpose of this paper is to derive such relationships and discuss their significance.

Before entering into details, a general comment on the thermodynamics of electrolytic systems is desirable. It is not thermodynamically possible to define the activity of an ion in a soil in the same way as for an uncharged molecule, without referring to some other quantity. The reason for this is that if the electric potential varies from point to point in a soil-soil-solution system, the activity of an ion will also vary. It is, however, not necessary to refer the activity of an ion to the electric potential. It can be shown that certain products and ratios of the activities of a pair of ions are the same at every point of the system when equilibrium is established. The ions Ca^{2+} and K^+ will serve as an example. In a given soil at a given moisture content the ratio $\sqrt{a_{Ca^{2+}}}/a_{K^+}$ will be the same at every point in the system, which includes all charged surfaces accessible for ion exchange and the whole of the solution. If a relatively small part of the solution is removed from the soil under such conditions that the equilibrium is not materially changed, this solution which can be regarded as homogeneous can be analysed for Ca^{2+} and K^+ and, with some approximation, $a_{Ca^{2+}}$ and a_{K^+} can be calculated. As the soil was in equilibrium with the solution the ratio $\sqrt{a_{Ca^{2+}}}/a_{K^+}$ must be the same in the soil as in the solution removed, but the individual activities of Ca^{2+} and K^+ may differ. One point of interest in this connexion is that if, for instance, a_{K^+} could be estimated at some point in the soil, then $a_{Ca^{2+}}$ could be calculated from the known ratio $\sqrt{a_{Ca^{2+}}}/a_{K^+}$ in the solution.

Similarly, when comparing Ca^{2+} and Cl^- the product $\sqrt{a_{Ca^{2+}}}.a_{Cl^-}$ is also the same in the soil as in the solution. Taking two ions of the same valency, such as K^+ and Na^+, the system soil-solution can be characterized by the ratio a_{K^+}/a_{Na^+}, and in the case of Na^+ and Cl^- by the product $a_{Na^+}.a_{Cl^-}$.

In practice it is convenient to express these relationships in logarithmic form, using p as the symbol for the negative logarithm of the activity in

the same way as in the pH. The quantities referred to above can thus be written

$$pCa^{2+}-2pK^{+},\ pCa^{2+}+2pCl^{-},\ pK^{+}-pNa^{+},\ pNa^{+}+pCl^{-},\ \&c.$$

The general forms for two ions of valencies V_1 and V_2 are

$$V_2\,pM_1-V_1\,pM_2, \qquad V_2\,pM_1+V_1\,pA_2,$$

where M is a cation and A an anion. This procedure is used for all the relationships derived in this paper.

Ions which are present only in exchangeable form are treated first, and then ions which are present as solid, well-defined compounds; the latter are subdivided according to whether they are independent or dependent on the oxidation-reduction potential of the soil. Unless otherwise stated, all data on solubility products, dissociation constants, and oxidation reduction potentials are taken from Latimer (1950).

I. *Exchangeable Ions*

From work on cation exchange equilibria (see a recent review by Eriksson, 1952) it has been found that the relationship between the activities of a pair of ions in a solution in equilibrium with a soil can for two ions of the same valency, e.g. K^+ and Na^+, be written

$$pK^{+}-pNa^{+} = pK+p\,\frac{[K]}{[Na]}. \qquad (1)$$

The square brackets denote total amounts present in exchangeable form and pK is a factor which, if the soil is reasonably homogeneous with respect to the clay fraction, will remain comparatively constant even if the ratio or the actual amount of [K] and [Na] is varied. In cases where the hydrogen ion is involved pK is, from all experimental evidence, no longer constant (Krishnamoorthy and Overstreet, 1950) but varies with the degree of saturation with ions other than the hydrogen ion.

For a di-monovalent pair such as Ca^{2+} and K^+ the corresponding relationship to (1) is written

$$pCa^{2+}-2pK^{+} = pK+p\,\frac{[Ca]}{[K]^2}\,[Ca+K+...]. \qquad (2)$$

The summation within the square brackets extends over all the species present, expressed in equivalents. pK may vary in this case also, but for many practical purposes it can be regarded as constant. A point of interest here is that the magnitude of pK seems to depend on the exchange capacity in the case of clay mineral fractions; the higher the exchange capacity, the higher pK. This is also expected when the system soil-solution is treated as a Donnan system.

From eqn. (2) it will be seen, for instance, that if a soil is percolated with a solution of a definite $pCa^{2+}-2pK^{+}$ (i.e. $\sqrt{a_{Ca^{2+}}}/a_{K^+}$ is kept constant) it will attain a definite composition which will not be altered as long as $pCa^{2+}-2pK^{+}$ in the percolating solution is kept constant. This

phenomenon has also been demonstrated experimentally by Schofield (1951), who has called it 'the ratio law'.

Equations like (1) and (2) which can be formulated for all exchangeable cations present in a soil are of great practical importance in connexion with the leaching and accumulation of exchangeable cations which can take place when irrigating soils by any natural waters. If pK for different pairs of ions is known for a certain soil as well as the amounts of exchangeable cations, changes in these due to irrigation can be predicted if the concentrations of the same cations in the irrigation water (after due correction for evaporation) are known. In this way it is possible to forecast whether a planned irrigation will turn the soil into an alkali soil or not.

II. *Ions present as Solid Compounds in Equilibrium*

(*a*). Ca *and* Mg *compounds*

If solid $CaCO_3$ is present in the soil it can be shown that

$$pCa^{2+}-2pH = -8{\cdot}4-pH_2CO_3 \tag{3}$$

This is derived from the solubility product of $CaCO_3$ (calcite) and the dissociation constants of H_2CO_3. Approximately one volume of CO_2 is soluble in one volume of water at one atmosphere pressure and ordinary temperature. Therefore

$$pH_2CO_3 = 1{\cdot}6+pCO_{2(g)} \tag{4}$$

and

$$pCa^{2+}-2pH = -10{\cdot}0-pCO_{2(g)}. \tag{5}$$

Hence at constant temperature the quantity $pCa^{2+}-2pH$ will depend only on the CO_2 pressure in the gas phase in equilibrium with the soil. The CO_2 concentration in the soil air is of the order of 0·1 per cent.; in soils therefore

$$pCa^{2+}-2pH = -13 \tag{6}$$

when solid $CaCO_3$ is present.

The value -13 can be regarded as a minimum value in any soil under field conditions.

A simple way to estimate $pCa^{2+}-2pH$ in a soil containing solid $CaCO_3$ is to determine its CO_2 tension and use eqn. (5) for the calculation of $pCa^{2+}-2pH$.

As $MgCO_3$ is more soluble than $CaCO_3$ it probably never exists in equilibrium in ordinary soils. $Mg(OH)_2$ is less soluble than $Ca(OH)_2$, but since

$$pMg^{2+}-2pH = -16 \tag{7}$$

when solid $Mg(OH)_2$ is present, *this* compound can hardly exist in soils.

The Ca phosphates will be treated in connexion with phosphates.

(*b*). Al^{3+} *and* Fe^{3+} *hydroxides*

These two are present in soils mainly as more or less hydrated oxides and also in combination with silica, phosphate, and humus. In the pH range prevalent in soils and in the presence of the hydroxides;

$$pFe^{3+}-3pH = -4{\cdot}6, \tag{8}$$

$$pAl^{3+}-3pH = -9{\cdot}3. \tag{9}$$

These values must be regarded as minimum values. In the presence of humate and silica they may be somewhat higher, but the order of magnitude is certainly correct.

There are also data available for the compounds $Fe(OH)^{2+}$ and $Al(OH)^{2+}$ which may be of interest. In the presence of the hydroxides

$$pFe(OH)^{2+} - 2pH = -2{\cdot}4, \tag{10}$$

$$pAl(OH)^{2+} - 2pH = -4{\cdot}4. \tag{11}$$

At pH 4, $pFe(OH)^{2+} = 5{\cdot}6$ and $pAl(OH)^{2+} = 3{\cdot}6$; their concentrations at this pH are thus quite low. Those of Fe^{3+} and Al^{3+} are, $pFe^{3+} = 7{\cdot}4$ and $pAl^{3+} = 2{\cdot}7$. As Al is believed to be toxic at low pH values it appears that the toxicity is most probably due to Al^{3+} which apparently reaches a relatively high concentration in this range. At higher pH values, however, $Al(OH)^{2+}$ dominates very much over Al^{3+}.

(*c*). $H_2PO_4^-$ *compounds*

The most probable forms of inorganic phosphate in soils are compounds of Fe^{3+}, Al^{3+}, and Ca^{2+}. In waterlogged soils the role of Fe^{3+} may be taken over by Fe^{2+}.

A well-known compound with Fe^{3+} is $Fe(OH)_2H_2PO_4$, sometimes written $FePO_4 . 2H_2O$. It seems to form in fairly acid systems where no $Fe(OH)_3$ is present. From Gaarder's (1930) data the solubility product is estimated to be 10^{-22} and this gives

$$pH + pH_2PO_4^- = 2{\cdot}8 - (pFe^{3+} - 3pH), \tag{12}$$

which seems to be valid when no $Fe(OH)_3$ is present. As the pH is raised $Fe(OH)_3$ will form, and $pFe^{3+} - 3pH$ should then be equal to $-4{\cdot}6$; from this it would be expected that

$$pH + pH_2PO_4^- = 7{\cdot}4 \tag{13}$$

should be valid. It is, however, known that at constant pH the presence of even a moderate excess of $Fe(OH)_3$ has a marked influence on the solubility of $Fe(OH)_2H_2PO_4$ (cf. Gaarder, 1930). This can only be explained as due to exchange with OH^- in $Fe(OH)_3$ which, when precipitated in cold, is highly reactive. Physical sorption of $H_2PO_4^-$ should not influence the phosphate solubility as long as $Fe(OH)_2H_2PO_4$ is present in solid form. The equilibrium in the presence of $Fe(OH)_3$ must be governed by the amounts of OH^- groups available for exchange as well as the amount of $H_2PO_4^-$ in exchange positions. The mixture of $Fe(OH)_3$ and $Fe(OH)_2H_2PO_4$ thus behaves as a solid solution and the equilibrium can be written

$$pH + pH_2PO_4^- = pK + p\frac{[H_2PO_4]}{[OH]}, \tag{14}$$

where pK may be somewhere around the value 7·4 in eqn. (13). The quantities in the square brackets denote the amounts of $H_2PO_4^-$ exchanged against OH^- on the $Fe(OH)_3$ and the amount of OH^- still available for exchange.

It should be noted that eqn. (14) is of the same form as eqn. (1).

For the corresponding Al compound $Al(OH)_2H_2PO_4$ Gaarder's (1930) data give $K = 10^{-19}$, therefore

$$pH+pH_2PO_4^- = -0{\cdot}2-(pAl^{3+}-3pH). \quad (15)$$

The behaviour in the presence of $Al(OH)_3$ seems to be the same as in the case of $Fe(OH)_2H_2PO_4$. Therefore

$$pH+pH_2PO_4^- = pK+p\frac{[H_2PO_4]}{[OH]}, \quad (16)$$

where pK may be of the order of 9, should give the relationship between the pH and $pH_2PO_4^-$ in the presence of $Al(OH)_3$.

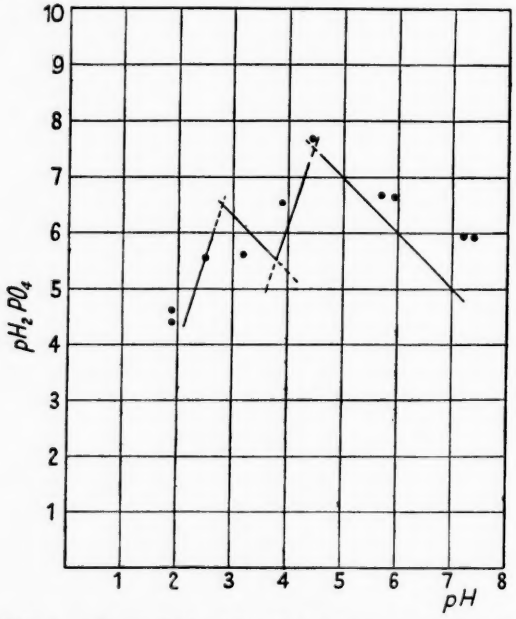

FIG. 1. A theoretical relationship between the pH and the $pH_2PO_4^-$ in presence of given amounts of Fe^{3+} and Al^{3+}. Filled circles, experimental data from a Scottish soil.

In order to illustrate what could happen in a system where Al^{3+}, Fe^{3+}, and $H_2PO_4^-$ are present, $pH_2PO_4^-$ has been calculated as a function of the pH in a system where Fe^{3+} and Al^{3+} are 10^{-2} molar and P as phosphate is 10^{-4} molar, with assumed values for the pK's. The result is shown in Fig. 1. For comparison actual solubility data† on phosphate from a Scottish soil derived from basic igneous rock drift is shown by the filled circles.

† The soil was shaken in distilled water with varying additions of HCl or KOH. Phosphate and pH were determined in the filtrate.

The relationships expressed by the four lines in Fig. 1 are, from left to right, the following.

The first line represents in its beginning eqn. (12) up to that pH where $Fe(OH)_3$ starts to precipitate, which in this case happens at pH 2·2. From that point the relation is given by eqn. (14), in which pH, $[H_2PO_4]$, and [OH] vary simultaneously. Above the point where practically all Fe^{3+} is precipitated [OH] and $[H_2PO_4]$ will remain practically constant; at that point the second line starts.

As the pH is increased Al^{3+} will start to precipitate some phosphate; this happens at the crossing between the second and third lines. The third line is represented by eqn. (15) up to that point where $Al(OH)_3$ starts to precipitate; above that point the third line (as well as the fourth) is represented by eqn. (16).

It should be noted that within the pH range of about 5 to 7 the ratio $[H_2PO_4]/[OH]$ in a soil will be practically constant, because the amount of $H_2PO_4^-$ in solution is of a much lower order of magnitude than that in the solid phase. A simplified and generalized expression for the relation between pH and $pH_2PO_4^-$ in the presence of $Al(OH)_3$ may then be obtained by writing

$$pH+pH_2PO_4^- = pK, \tag{17}$$

where pK may be altered by altering the ratio $[H_2PO_4]/[OH]$ in the soil although not necessarily in the quantitative way expressed by eqn. (16), as in the pH range prevalent in soils the ferric phosphates should be very much hydrolysed.

From Fig. 1 it seems likely that $Al(OH)_3$ plays by far the most important role in 'phosphate fixation' in soils. A discussion of different means of altering $pH_2PO_4^-$ in eqn. (17) may therefore be interesting. From this equation it will be seen that if pK remains constant $pH_2PO_4^-$ will be decreased if pH is increased. This may actually happen when a soil is limed. If the pH is kept constant $pH_2PO_4^-$ can be decreased by decreasing pK, which can be done in two ways. Firstly it can be decreased by increasing $[H_2PO_4]$, the fixed phosphate, by heavy application of phosphate fertilizers. Secondly, [OH] can be decreased by increasing the organic matter content of the soil which displaces OH^- in the $Al(OH)_3$ and thereby causes pK to decrease.

The third group of phosphates, namely, calcium phosphates, are believed to exist in 'neutral' soils. There is surprisingly little definite known about these compounds. Latimer has quoted Britton's estimate from Basset's data and gives for $CaHPO_4.2H_2O$

$$pCa^{2+}+pHPO_4^{-2} = 5{\cdot}3 \tag{18}$$

and for $Ca_3(PO_4)_2$

$$3pCa^{2+}+2pPO_4^{-3} = 25. \tag{19}$$

If written in terms of $pH_2PO_4^-$ eqns. (18) and (19) become

$$\tfrac{1}{2}pCa^{2+}+pH_2PO_4^- = -1{\cdot}9-\tfrac{1}{2}(pCa^{2+}-2pH) \tag{20}$$

$$\tfrac{1}{2}pCa^{2+}+pH_2PO_4^- = -6{\cdot}71-(pCa^{2+}-2pH). \tag{21}$$

In Fig. 2, $\frac{1}{2}pCa^{2+}+pH_2PO_4^-$ is plotted against $pH-\frac{1}{2}pCa^{2+}$ using the above equations and the relationship is represented by the full-drawn line. For comparison data given by Benne, Perkins, and King (1936) and by Teakle (1938) are shown represented by circles. Benne, Perkins, and

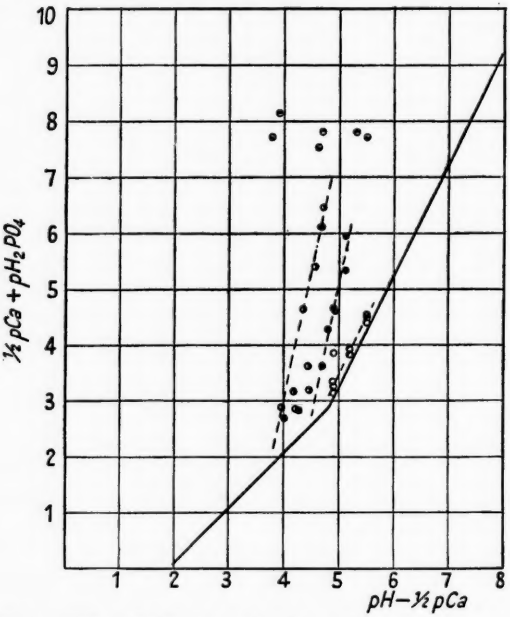

FIG. 2. The solubility relationships of some Ca phosphates. Full drawn line $CaHPO_4$ and $Ca_3(PO_4)_2$ according to their solubility products.

◑ Experimental data of Benne, Perkins, and King.
● Experimental data of Teakle, low Ca concentration.
○ Experimental data of Teakle, high Ca concentration.
◓ Experimental data of a Scottish soil, Greenhall. No phosphate. Increasing amounts of lime in the field from left to right.
◒ Experimental data of a Scottish soil, after application of superphosphate in the field.

King's data deviate most and point to a Ca phosphate much more insoluble than $Ca_3(PO_4)_2$. Teakle has two sets of values; in one the Ca concentration was kept relatively low and it will be seen that this set shows the same trend as Benne, Perkins, and King's values although the compound seems to be somewhat more soluble. In the second set a large excess of Ca^{2+} was used; these values correspond very nearly to the $Ca_3(PO_4)_2$ compound.

These data thus give a rather confusing picture of the solubility of Ca phosphates. This can be explained as due to the formation of a solid solution between $CaHPO_4.2H_2O$ and $Ca_3(PO_4)_2$. In Teakle's series where the Ca^{2+} concentration was kept low, the precipitation of phosphate by adding NaOH must have started with the formation of

$Ca_3(PO_4)_2$. As the Ca^{2+} was consumed, however, the conditions for the formation of $CaHPO_4.2H_2O$ became more favourable; $pH-\frac{1}{2}pCa^{2+}$ decreased to the region where $CaHPO_4.2H_2O$ should be formed and the precipitation ended up in a mixture of $CaHPO_4.2H_2O$ and $Ca_3(PO_4)_2$. If this mixture formed a solid solution, this could account for the decreased solubility since, in that case, the activity of $CaHPO_4.2H_2O$ and $Ca_3(PO_4)$ should be less than unity.

It should be mentioned that phenomena such as the formation of a mixed compound between $CaHPO_4.2H_2O$ and $Ca_3(PO_4)_2$ have been observed earlier and it has also been suggested that they form solid solutions (see Mellor, 1923).

It may also be of interest to note that if the molar proportions of $CaHPO_4.2H_2O$ and $Ca_3(PO_4)_2$ are equal the resulting precipitate can be written $Ca_4H(PO_4)_3.2H_2O$, which is known as calcium octophosphate. Recent data on the solubility of this compound has been given by Bjerrum (1936).

The six points in the upper part of Fig. 2 are calculated from data for water extracts from limed and unlimed soil, treated and untreated with phosphate in the field. It will be seen that liming has decreased the quantity $\frac{1}{2}pCa+pH_2PO_4^-$ (Schofield's (1949) phosphate potential) in both the treated and untreated soil. The bigger dressing of lime has, however, not given any further decrease. This could be taken as an indication of formation of some Ca phosphate in this case, or as an indication that the phosphate present is mainly physically adsorbed. The second alternative is interesting because if this were true then the result of liming should be a transformation of exchangeable into adsorbed phosphate.

(*d*). Fe^{2+} *and* Mn^{2+}

The ions treated so far have either been independent of the oxidation-reduction potential in the soil or, as in the case of iron, have been considered only in the higher valency state. There are two other ions, namely Fe^{2+} and Mn^{2+}, which are greatly influenced by the oxidation-reduction potential of the soil. These will be treated further.

The variation in the oxidation-reduction potential with the pH for some of the main inorganic oxidation-reduction couples occurring in soils are shown in Fig. 3, the activity of the soluble components being taken as unity. The data for solubility products and standard oxidation-reduction potentials are taken from Latimer. The way the curves are arrived at is shown by the following example:

For the $Fe^{2+}-Fe^{3+}$ couple the standard E value is $-0{\cdot}771$ volt.

If the activities of Fe^{2+} and Fe^{3+} are $a_{Fe^{2+}}$ and $a_{Fe^{3+}}$, respectively, then at 25° C.

$$E = -0{\cdot}771-0{\cdot}059 \log \frac{a_{Fe^{3+}}}{a_{Fe^{2+}}}, \qquad (22)$$

which also can be written

$$E = -0{\cdot}771-0{\cdot}059(pFe^{2+}-pFe^{3+}). \qquad (23)$$

At unit activities E is apparently $-0{\cdot}771$ and independent of pH up to

that point where $Fe(OH)_3$ starts to precipitate, which should happen at pH = 1·53. At higher pH, $pFe^{3+} - 3pH = -4{\cdot}6$, eqn. (11), which changes the equation to

$$E = 10{\cdot}771 - 0{\cdot}059\,(pFe^{2+} + 4{\cdot}6 - 3pH) \qquad (24)$$

and is represented in the figure by the sloping part ($pFe^{2+} = 0$). Above pH7, $Fe(OH)_2$ starts to precipitate, which alters the slope in this region.

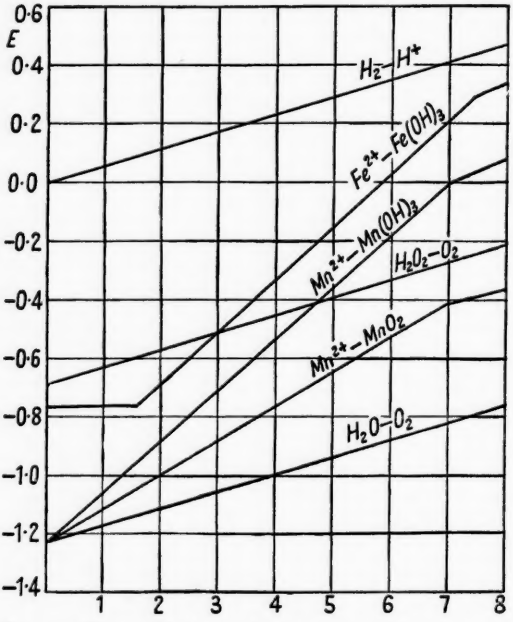

FIG. 3. The oxidation-reduction potentials of some couples as a function of the pH.

From the figure it will be seen that both Fe^{2+} and Mn^{2+} should be oxidized by oxygen (the H_2O—O_2 couple) at all pH except for very low pH with Mn^{2+}. It is well known that Fe^{2+} is easily oxidized by oxygen but Mn^{2+} is much stabler in solution. In a soil, however, there is always a microflora which can act as catalyst for the oxidation and utilize the energy released. It will be seen that, except at low pH values, the oxidation of Mn^{2+} to $Mn(OH)_3$ would release more energy than the oxidation of Mn^{2+} to MnO_2. This makes the dismutation process

$$2Mn(OH)_3 = Mn^{2+} + MnO_2$$

very unlikely at higher pH values and at higher Mn^{2+} concentrations. If this dismutation process is written in full it reads

$$2Mn(OH)_3 + 2H^+ = Mn^{2+} + MnO_2 + 4H_2O,$$

which shows that it should be favoured by a low pH. This can also be

concluded from the figure. At very low pH values both oxides are unstable with respect to decomposition by water as they oxidize the water to oxygen.

As the oxygen in a soil can be supplied in practically infinite quantities the E of a soil will be governed completely by the H_2O—O_2 couple provided O_2 has free access to the soil. Then at any pH

$$E = -1{\cdot}229 + \frac{0{\cdot}059}{4} pO_{2(g)} + 0{\cdot}059\ pH. \qquad (25)$$

The tendency for all other oxidation-reduction systems is to attain this potential. At equilibrium, therefore, E for the Fe^{2+}—$Fe(OH)_3$ couple must be equal to that of oxygen; at a given pH, this can only happen at a definite pFe^{2+}. In this way pFe^{2+} can be expressed as a function of the pH and pO_2 by combining the two equations and the resulting expression reads:

$$pFe^{2+} - 2pH = 3{\cdot}16 - 0{\cdot}25pO_{2(g)}. \qquad (26)$$

If the partial pressure of oxygen is 0·2 atmosphere, then

$$pFe^{2+} - 2pH = 3{\cdot}0. \qquad (27)$$

For the two Mn couples the same procedure gives

$$pMn^{2+} - 2pH = -0{\cdot}1 - 0{\cdot}25pO_2 \ (Mn(OH)_3 \text{ present}), \qquad (28)$$

$$pMn^{2+} - 2pH = -0{\cdot}0 - 0{\cdot}5pO_2 \ (MnO_2 \text{ present}). \qquad (29)$$

From this it follows that $Mn(OH)_3$ should be the less stable form at the equilibrium. According to Latimer, however, the potential for the Mn^{2+}—$Mn(OH)_3$ couple is rather approximate; he states that it is probably correct to within 0·1 volt, which means that the constant −0·1 is correct within 4 units. From observations on natural minerals, however, it can be concluded that the mineral MnOOH which is a partly dehydrated form of $Mn(OH)_3$ seems to be converted slowly to pyrolusite. Further, compounds of 4-valent manganese are much more common in nature than those of the trivalent form. Dismutation of $Mn(OH)_3$ may then occur at the normal pressure of oxygen provided that the Mn^{2+} formed is oxidized. It may be safe to conclude that in freely drained soils most probably

$$pMn^{2+} - 2pH = 0. \qquad (30)$$

One of the naturally occurring oxides of manganese is hausmannite, Mn_3O_4. There are no data available on this. It seems to be rather inert against reducing agents (cf. Jones and Leeper, 1951), which, of course, is no proof that it is more insoluble than the other types; it may merely be relatively slow reacting. Whether it occurs in natural soils is uncertain.

With regard to Mn^{2+} and also Fe^{2+} in soils, it should be added that there is a steady oxidation-reduction process going on in a soil whereby organic matter is converted partly into stabler organic compounds and partly into CO_2. It is obvious that both Fe and Mn can take part in this process so that the actual amounts circulating through the lower oxidation stages may be considerable.

Under reducing conditions Mn^{2+} and Fe^{2+} may increase considerably. It may be of some interest to treat such a system with respect to phosphate, as vivianite sometimes occurs in waterlogged soils.

There are no data available on vivianite, but the author has determined the solubility† and estimated the solubility product to be such that

$$pH+pH_2PO_4^- = -6{\cdot}0-1{\cdot}5(pFe^{2+}-2pH). \quad (31)$$

If pFe^{2+} is 2, then at pH6, $pH_2PO_4^-$ would be 3·0, so that the compound is not very stable. If H_2S is present, as it often is in waterlogged soils, there will be a competition between H_2S and $H_2PO_4^-$ for the ferrous ion. From the solubility product of FeS and the dissociation constants of H_2S

$$pFe^{2+}-2pH = -2{\cdot}94-pH_2S, \quad (32)$$

which when combined with eqn. (31) gives

$$pH+pH_2PO_4^- = -1{\cdot}6+1{\cdot}5pH_2S. \quad (33)$$

If pH_2S is 4 (a relatively high figure), then at pH6, $pH_2PO_4^-$ would be $-1{\cdot}6$, which corresponds to a 4-molar $H_2PO_4^-$ concentration in a soil.

In the presence of oxygen eqn. (28) gives $pFe^{2+}-2pH = 3{\cdot}0$. From this

$$pH+pH_2PO_4^- = -10{\cdot}5,$$

which shows that it cannot exist in well-drained soils. It is not surprising that vivianite is rather rare, even in waterlogged soils, because such soils generally contain sulphur compounds.

III. *Discussion*

In this paragraph a few points of interest relating to the equations shown in the preceding paragraphs will be discussed.

Firstly it must be borne in mind that all the equations refer to equilibrium states and that it is by no means certain that physico-chemical changes in a soil *in situ* take place near the equilibrium. If they take place *far* from the equilibrium state other physico-chemical factors such as rate of reaction, rate of dissolution, and rate of diffusion have to be considered. This is probably more important in the case of oxidation-reduction processes in soils than in other reactions as the microbes, which take part in the oxidation-reduction processes, may have a great influence on such a factor as rate of reaction.

Some of the equations relating to phosphate are hypothetical as they rest on the assumption of the formation of solid solutions of two solid compounds. As is pointed out in the text, they may at least reflect the qualitative behaviour of the phosphate in soils. Further experimental work is, however, needed in order to assess the validity and usefulness of the concept of solid solutions in soils.

† The compound $Fe_3(PO_4)_2.8H_2O$ was prepared from a solution of phosphate and ferrous sulphate in presence of sulphite. It was identified by Miss A. Milne in the X-ray Department of the Institute.

A very common word, especially in connexion with phosphate in soils, is *adsorption* or more generally *sorption*, by which is meant the process of removal of phosphate ions from a solution by a soil suspended in the solution. The process can, however, be divided into two separate processes which do not involve the formation of definite compounds. One is a physico-chemical process by which hydroxyl ions are exchanged against phosphate ions. The hydroxyl groups may belong to sesquioxides in soils. The other process is purely physical; phosphate ions are attached to the soil particle surfaces by physical forces such as van der Waals forces. In this case a new fixed charge is created for each attached phosphate ion. This process has not been considered here. Although it may be of great importance in laboratory work with soils where phosphate adsorption is often studied with the addition of relatively great amounts of phosphate, it is the author's opinion that this process is of but little importance in soils *in situ*, where the concentration of phosphate in the soil solution is generally very low. In any case physically adsorbed phosphate, if present, does not invalidate the equations involving the phosphate ion.

IV. *Summary*

The physico-chemical behaviour of the common ionic nutrients in soils has been examined on the basis of a series of relationships derived from existing data on pH, solubility products, dissociation constants, and oxidation-reduction potentials. The probability of formation of various compounds and the order of magnitude of the equilibrium concentrations of different nutrients under varying soil conditions have been assessed.

V. *Acknowledgement*

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REFERENCES

BENNE, E. J., PERKINS, A. T., and KING, H. H. 1936. The effect of calcium ions and reaction upon the solubility of phosphorus. Soil Sci. **42**, 29–38.

BJERRUM, N. 1936. Undersøgleser over Kalciumfosfaters Opløslighed. Nordiska (19:e Skandinaviska) Naturforskarmötet i Helsingfors, 344–8.

ERIKSSON, E. 1952. Theories of cation exchange on clay minerals. Soil Sci. (In the press.)

GAARDER, T. 1930. Die Bindung der Phosphorsäure im Erdboden. Die Löslichkeit der Phosphorsäure in wässerigen Elektrolytlösungen bei wechselndem pH-Wert und Kationen-Inhalt. Medd. nr. 14 fra Vestlandets Forstlige Forsøksstation. Bergen, 1930.

JONES, L. H. P., and LEEPER, J. W. 1951. The availability of various manganese oxides to plants. Plant and Soil, **3**, 141–53.

KRISHNAMOORTHY, C., and OVERSTREET, R. 1950. Behaviour of hydrogen in ion-exchange reactions. Soil Sci. **69**, 87–93.

LATIMER, W. M. 1950. The Oxidation States of the Elements and Their Potentials in Aqueous Solutions. New York. (Rev. ed.)

MELLOR, J. W. 1923. A Comprehensive Treatise on Inorganic and Theoretical Chemistry, vol. **3**, p. 884. London.

SCHOFIELD, R. 1949. Thermodynamic potentials of soil constituents. Rothamsted Expt. Stat. Rep. 1949, p. 29.

—— 1951. A ratio law governing the equilibrium of cations in soil solution. Proc. Eleventh International Congress of Pure and Applied Chemistry, **3**, 257–61.

TEAKLE, L. J. H. 1928. Phosphate in the soil solution as affected by reaction and cation concentrations. Soil Sci. **25**, 143–62.

WADSLEY, A. D., and WALKLEY, A. 1940. Some observations on the potential of the manganese dioxide electrode. J. Electrochem. Soc. **95**, 11–20.

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THE TECHNIQUE OF DIFFERENTIAL THERMAL ANALYSIS (DTA)

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I. THE QUANTITATIVE ASPECT

A. *Introduction*

In the Differential Thermal Analysis of soils we encounter four main types of heat reactions whose nature has a direct bearing on the reaction peaks:

(*a*) Internal reactions which do not involve equilibrium of the reacting mass and its products with the external atmosphere.
(*b*) Internal reactions in which gaseous products are released and the shape and size of resulting peak is influenced by the diffusibility of these products through the packing.
(*c*) Reactions which involve the participation of an external reactant, for example, atmospheric oxygen.
(*d*) Reactions which involve the release of gaseous products in addition to the participation of an external gaseous reactant.

The use of this method for quantitative analysis is therefore limited unless the details of procedure can be reproduced within the limits of experimental error in each run. We are thus restricted at the very start to reactions of internal type when using standard equipment.

For a characteristic peak, there are three measurable quantities which could be of assistance in such analysis: (*a*) the height, (*b*) length, and (*c*) area of the peak.

The length of the base measurements are, however, subject to the condition that practically no change in thermal characteristics of the material take place during the reaction.

Jeffries (1944) has investigated the significance of the height of the peak. He concludes that provided the amounts of the inert material and active sample used are thermally equivalent, the percentage increases in the apparent specific heat at the maximum of, say, the endothermic peak of kaolinite are directly proportional to the composition of mixtures of kaolinite and inert materials. He has also shown that this percentage increase is independent of the inert diluent. The results he has given seem to justify this completely empirical approach, but the sensitivity and value of this procedure are not very different from that of determining peak areas. It has the added disadvantage of requiring reliable data for the specific heats of various materials over a large range of temperature.

Speil and co-workers (1945) have derived an expression which shows the area of a characteristic peak to be directly proportional to the mass of active material in a mixture and the heat of reaction per gramme of material, and inversely, to an undefined geometrical constant and the

thermal conductivity of the mixture. This theory, together with Kerr and Kulp's modification (1948) and Dean's (1947) suggested relationship between the cosecant of the peak angle and the mass of reacting material, are highly simplified versions of a problem complicated by several factors. Each of these factors can vitiate the results of an error large enough to make their experimental verification impossible.

The problem here is one in which several rate-forming factors are introduced into the idealized case of the simple calorimeter, in which, for a definite heat of reaction and constant specific heat, the temperature change is independent of the amount of material. This latter condition does not hold in practice due to four principal factors: (*a*) thermal diffusivities of the sample, the specimen block, and the thermocouples; and (*b*) the response and sensitivity of the differential temperature recording device. If the combination of these factors is not a happy one, it may not be possible to detect a particular heat reaction, and the degree of resolution of consecutive heat reactions may be limited.

B. *Apparatus*

A Kent Multelec potentiometric recorder, having a full-scale deflexion of 0–15° on the lowest scale, was used in conjunction with a ceramic block. This had two triangle RR alumina crucibles of 0·5 ml. capacity buried in it to receive the active and inert samples. Chromel-alumel thermocouples of 28 s.w.g. wire were inserted to record temperature differences, their tips lying at the centre of the crucible.

C. *Relation between Mass of Active Material and Peak Area*

(*a*) *Experimental*

(i) Peak areas of the 600° C. endothermic reactions of kaolinite from a series of runs with varying amounts of the pure material were measured. (ii) Mixtures of DTA kaolinite (standard) and calcined kaolin were made up in various proportions and on these two separate sets of runs were carried out. In one set, the amount of material (450 mg.) used completely filled the sample hole; in the second, 200 to 250 mg. of material was used. This quantity is just above the range where the influence of the surface-area : volume ratio of the sample is most acute. In order to concentrate small amounts of the sample around the thermocouple point it is packed between layers of inert material.

(*b*) *Discussion*

The 'peak area : mass' curve for kaolinite (Fig. 1) shows that the surface area : volume ratio of the sample considerably influences the departure from true calorimetric conditions. Quasi-calorimetric conditions should therefore be obtained, by using very large samples. A limit, however, is placed on the maximum amount which can be used because of the necessity of establishing a favourable equilibrium between two opposing heat transfers—from the sample to the container-block, and from the sample to the thermocouple. Since the reaction begins at the boundary

between the sample and the block, the initial temperature gradients for both heat transfers have a common limit at the sample boundary. The farther removed this boundary is from the thermocouple, the more difficult it is to obtain a complete record of the heat change in the total sample. An optimum amount of material must be used in a DTA run to fulfil the latter requirements.

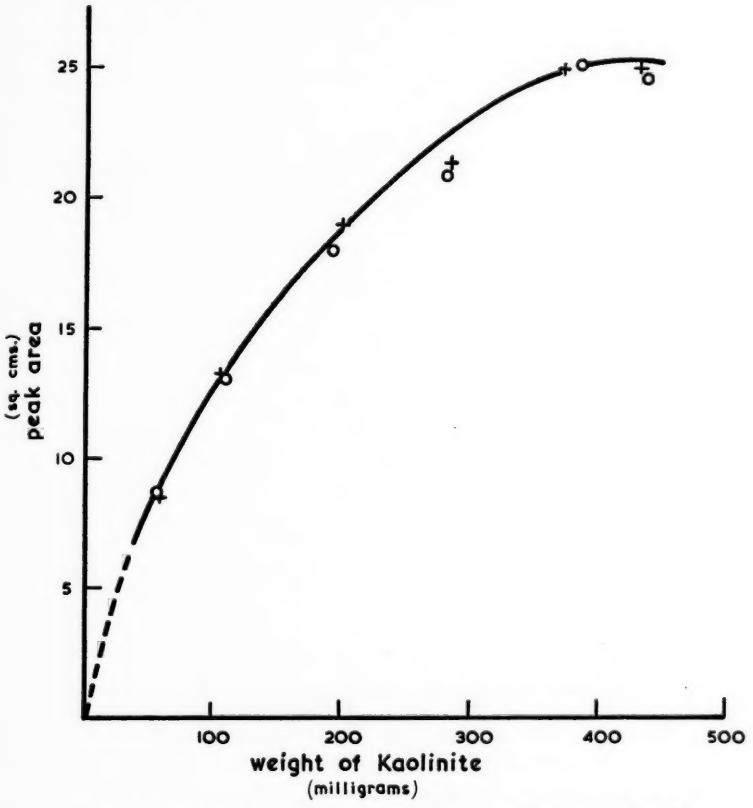

FIG. 1. DTA standard kaolinite; endothermic reaction (595–625° C.).

The selection of this particular weight to represent an optimum weight is, admittedly, quite arbitrary, but in the absence of complete data on the thermal diffusivities of the materials involved, it is the best way to demonstrate the validity of the argument.

With *kaolinite:inert-material mixtures*, peak areas of the 600° C. endothermic reaction, when plotted in terms of absolute weights of kaolinite in each mixture (Fig. 2), show that the peak areas obtained in the second set are much larger than those obtained in the first. Even so, the peak

areas in the second set are smaller than those obtained with equivalent amounts of the pure mineral.

Schafer and Russell (1942) had observed that peak areas are halved if the sample is distributed in a mixture although they did not try to interpret this on the basis of the volume of the sample. Our results suggest

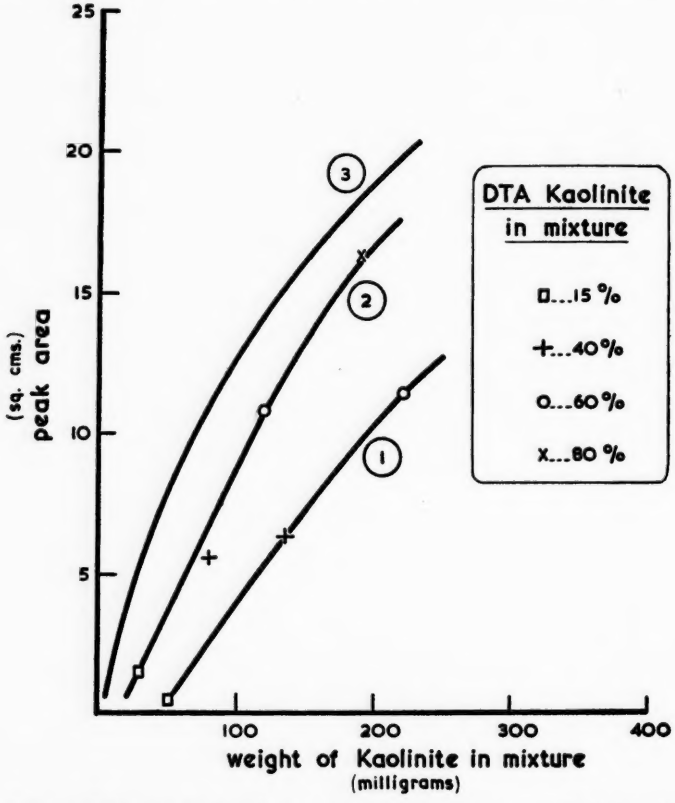

FIG. 2. DTA standard kaolinite: calcined kaolin mixtures. Endothermic reaction (595–625° C.). Curve 1. Total weight of active material—200 mg. 'sandwich'-packed. Curve 2. Total weight of active material—430 mg. full crucible. Curve 3. Reproduced from Fig. 1.

that the present set-up in DTA does not lend itself to the use of peak-areas as an absolute method for determining the proportion of a mineral in a mixture. With proper insulation of the sample holes such a correlation might not be impossible. For instance, it would be interesting to see the results of experiments conducted on similar lines with crucibles suspended in the middle of a furnace. Any alternative to the existing method of a set of runs of calibration mixture for each combination

of components would be a great time-saving factor in DTA technique.

D. Resolution of Closely Separated Reactions with the Same Sign

(a) Experimental

Varying quantities of calcium-saturated montmorillonite ($< 0{\cdot}2\mu$ fraction from Wyoming bentonite) equilibrated to 50 per cent. relative humidity were used for these runs. The packing procedure was the same as before, with the modification that the inert sample hole held a layer of fired bentonite between two layers of fired bayerite.

(b) Discussion

An important corollary to the use of an optimum amount of material is the effect on the resolution of reactions which occur at small temperature intervals. Good examples of this are the low-temperature endothermic

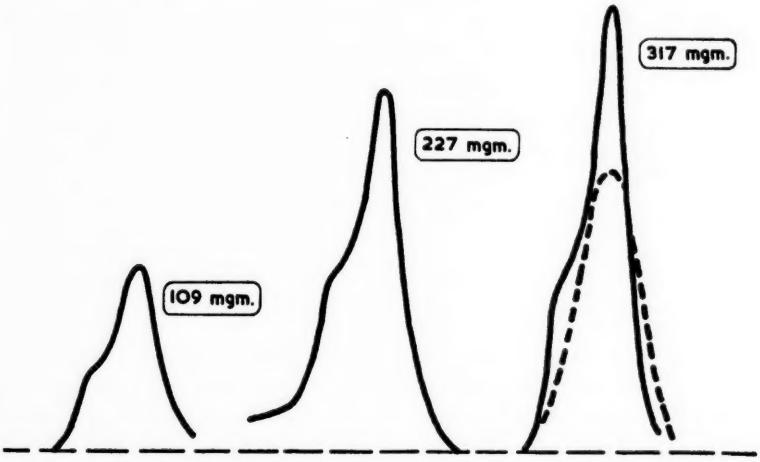

FIG. 3. Low-temperature endothermic peaks (100–200° C.) for calcium montmorillonite equilibrated to 50 per cent. relative humidity. Full line, 'sandwich'-packed; dotted line, full crucible.

peaks of calcium montmorillonoids which have been previously equilibrated to a high relative humidity. If the distance d of the sample-block boundary from the thermocouple is large enough, the reaction which occurs at the higher temperature T_2 will begin at the sample boundary at a time when the lower temperature T reaction is starting to occur at a distance x from the centre. x is therefore proportional to the thermal diffusivities of the sample and the block, and thus to d. The range of temperature over which a peak occurs is known to be inversely proportional to the rate of temperature increase of the furnace. However, using a fixed rate of temperature rise, the mass and hence the volume of the sample influences this range. The use of an optimum weight of material

is, therefore, an important consideration when the resolution of such peaks is to be considered.

A comparison of the low-temperature endothermic peaks of calcium montmorillonite (Fig. 3) under the two separate methods of packing illustrates the point. With the new method of packing (i.e. an optimum amount of active material between layers of inert material) there is also an increased resolution of peaks with decreasing amounts of material. Similar results (not reproduced) are obtained with closely separated endothermic reactions in the pyridine-montmorillonite system. We have not investigated whether this 'sandwich'-packing has the temporary effect of providing a constant vapour pressure over the active sample and so effectively helping in the resolution of two such peaks. It is difficult to see how such a coarse-grained packing can act as a tight cover at elevated temperatures, although one realizes that here a dynamic equilibrium between two rate-forming processes has to be considered.

II. ORGANIC COMPLEXES OF CLAYS

A. *Introduction*

It is generally accepted that in the combustion of organic compounds a sharp endothermic reaction (due to dehydrogenation) followed instantaneously by a strongly exothermic reaction (due to oxidation of released hydrogen) occur 100–200° C. after the removal of the water of hydration of the compound. In fact, the transition between the two reactions is so sudden that where the recording device has too slow a response, it is difficult to pick up the sharp endothermic reaction. A further exothermic reaction occurs at a much higher temperature due to conversion of the carbon to carbon dioxide.

Bradley and Grim (1948) have by DTA studies shown the difference between a base-exchange complex and a pure adsorption complex of montmorillonite using dodecylamine and the dimethyl ether of ethylene glycol. With the latter there is no broad high-temperature exothermic peak corresponding to the oxidation of carbon to carbon dioxide (Fig. 4). There is a general shift of all exothermic peaks in the base-exchange complex towards higher temperatures by 50–100° C., as compared with those in the ethylene glycol complex. Allaway (1949) obtained an ill-defined endothermic peak between 200° and 300° C. with glycerol, with a slight exothermic reaction up to 500° C. It seems, therefore, that organic compounds which are bound by non-ionic forces are released and oxidized below 500–600° C. Allaway claims that using piperidine, an organic base with a closed-ring structure, it is possible to show up differences in the DTA curves of clay complexes (Fig. 5) so clearly that it may be possible to use the method for detecting small amounts of montmorillonoids in admixture with kaolinite.

X-ray examination of their organic complexes by Bradley and Grim between 280° and 400° C. suggests the interlamellation of coke and silicate sheets which is more complete in the case of protein-clay complexes.

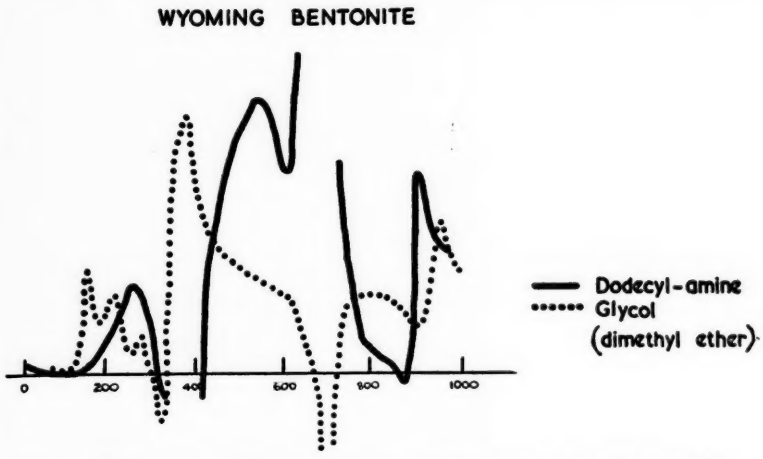

FIG. 4. DTA curves of a base-exchange complex and the adsorption complex of a polar molecule with montmorillonite (Bradley and Grim, 1948).

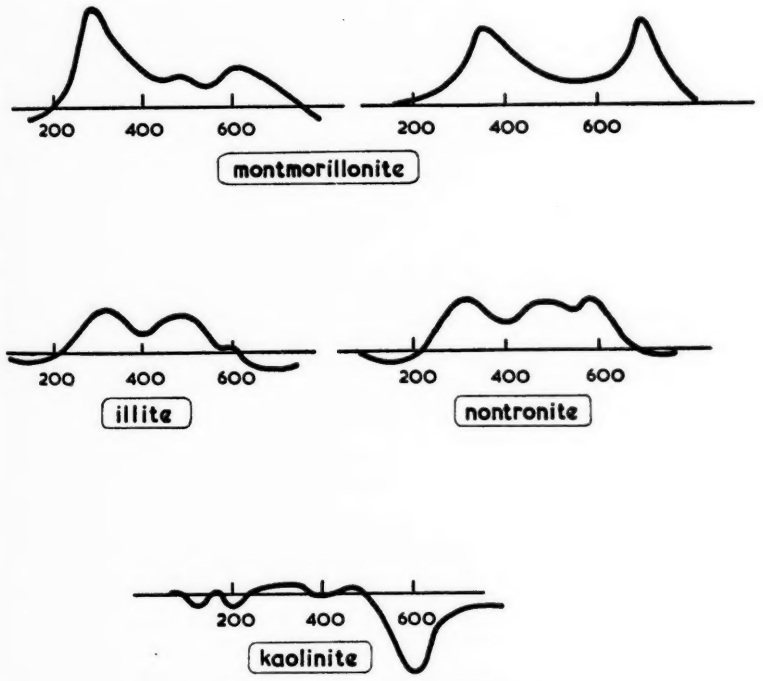

FIG. 5. Piperidine-clay complexes (Allaway, 1949).

B. *Experimental*

The method of 'sandwich'-packing was used and the active material was packed around the thermocouple tip between layers of fired bayerite. The inert material was an equivalent amount of calcined Wyoming bentonite between layers of fired bayerite. All samples were equilibrated to 50 per cent. relative humidity. The mixtures were prepared by fine-grinding the constituents for half an hour in an agate mortar.

C. *Discussion*

DTA curves of mixtures (Fig. 6) show the presence of a group of very pronounced exothermic peaks in the region 300–600° C. invariably consisting of two or more sharp peaks. Amorphous carbon and graphite

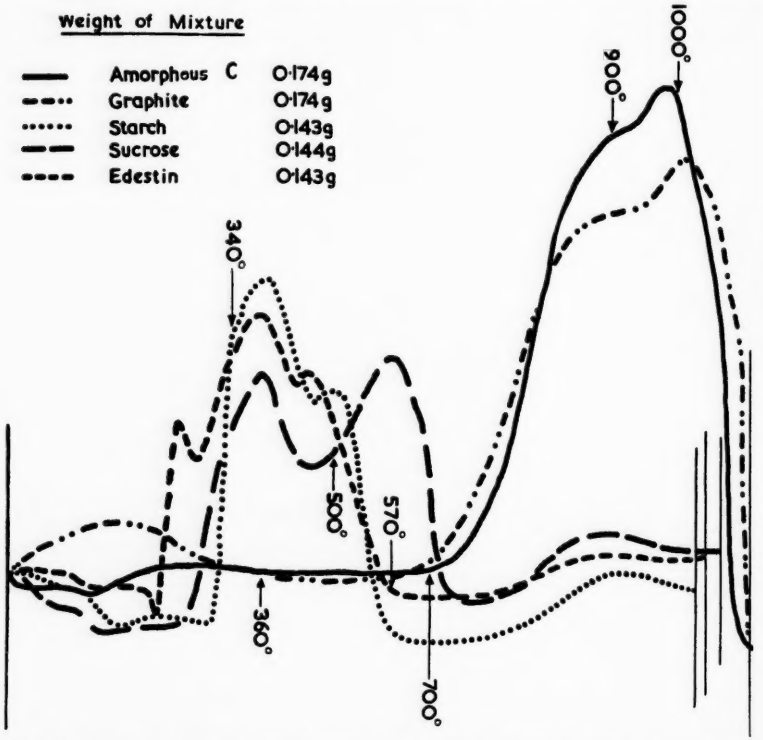

FIG. 6. 10 per cent. mixtures of organic material with fired Wyoming bentonite.

give exothermic peaks at 900–950° C. The corresponding high-temperature peak for the organic compounds occurs at 900°, but is small compared with the average figure of 2–5 per cent. carbon one would expect after carbonization. This suggests that in mixtures of montmorillonoids and organic compounds, complete combustion takes place, under the

conditions of the standard DTA runs, below 600° C. Organic compounds attracted to the clay sheet primarily by base-exchange show different characteristics in their DTA diagrams. Two large exothermic peaks appear whose relative positions depend on the strength with which the organic compounds are held in the interlamellar space. Thus the amine-clays (Fig. 5) give exothermic peaks about 300° and 550–700° C., whilst the protein-clay (Fig. 7) shows peaks at 600° and 900° C. approximately.

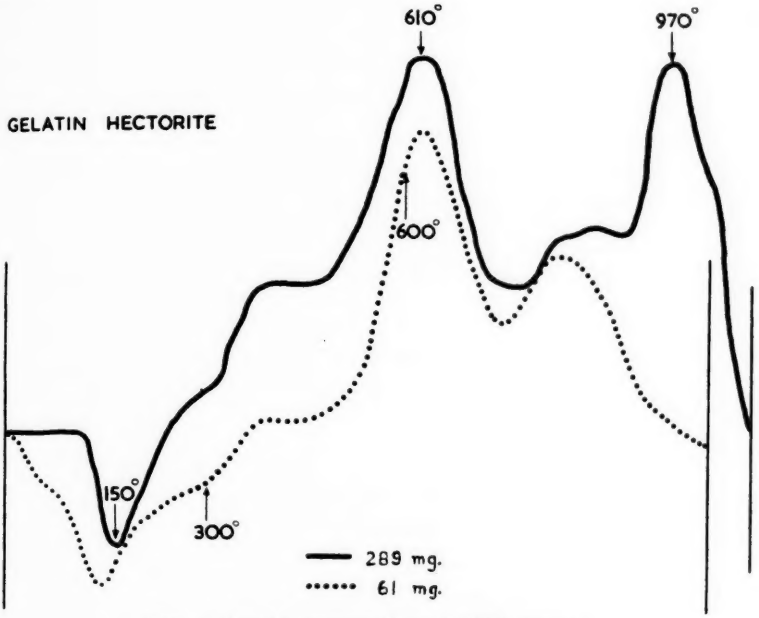

FIG. 7. Protein-montmorillonoid DTA curves.

In the light of this evidence it is of considerable interest to compare Figs. 6 and 7 and emphasize the following significant points: (1) The low-temperature endothermic peak in Fig. 7 is due to physically sorbed water in the interlamellar spaces of the complex. Its area is reduced to one-third of that of an equivalent amount of a mixed sodium-hydrogen montmorillonite, prepared under identical conditions. This illustrates the hydrophobic character of the protein-clay complex. (2) The initial endothermic peak due to dehydrogenation does not appear in our curves with the exception of the edestin-mixture. This must be due to the slower response of our recording device. (3) The first high-temperature exothermic peak appears at a higher temperature (> 600° C.) in the complex than in the mixture (300–550° C.) due to the close packing of the protein in the interlamellar spaces. The amorphous carbon and graphite mixtures do not exhibit this peak. (4) The second high-

temperature peak does not appear on the curves of the organic compound mixtures but appears at 900–1,000° C. on the curves of graphite and amorphous carbon mixtures.

This experimental evidence affords direct confirmation of the hypothesis that on heating complexes of montmorillonoids with large organic molecules which are strongly held in the interlamellar space, dehydrogenation and dehydration occur at or below 600° C. This results in a carbonized product in which layers of amorphous carbon (or even graphite) alternate with silicate sheets. At 900° C. the small endothermic reaction due to the final breaking up of the silicate sheets is masked by the initiation of a large exothermic reaction due to the complete combustion of the free carbon. In any consideration of these critical temperatures, it must be remembered that (*a*) these reactions are recorded as the temperature is increased at 10° C. a minute, and (*b*) a constant air-flow is not maintained over the sample during the run.

It is suggested that these factors should be borne in mind in the differential thermal analysis of untreated soil-clays.

Acknowledgement

Mr. W. A. Mitchell was responsible for assembling the apparatus outlined in Part I B.

REFERENCES

Allaway, W. H. 1949. Proc. Soil Sci. Soc. Amer. **13,** 183.
Bradley, W. F., and Grim, R. E. 1948. J. Phys. Coll. Chem. **52,** 1404.
Dean, L. A. 1947. Soil Sci. **63,** 95.
Jeffries, C. D. 1944. Proc. Soil Sci. Soc. Amer. **9,** 86.
Kerr, P. F., and Kulp, J. L. 1948. Amer. Miner. **33,** 387.
Schafer, G. M., and Russell, M. B. 1942. Soil Sci. **53,** 353.
Speil, S., Berkelhamer, L. H., Pask, J. A., and Davies, B. 1945. U.S. Bureau of Mines, Tech. Paper 664.

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THE ESTIMATION OF THE LIME REQUIREMENTS OF SOILS

SOIL AND CROP YIELD DATA FROM THE HARPER ADAMS AND OTHER LIMING EXPERIMENTS

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Introduction

It has been known from time immemorial that some soils are made much more productive when they are limed, but just how much lime to apply must always have presented a problem. One of the earliest attempts to give a quantitative expression to the lime requirement of a soil was by A. D. Hall (1905), where he stated that 'any soil containing less than one per cent. calcium carbonate will be benefited by liming'. No one today would accept this as an adequate definition of the need for lime, but it is interesting because it illustrates one approach to the problem, namely the estimation of the amount of calcium actually present in the soil either as free carbonate or in the exchangeable form.

With the development of the concepts of pH and base exchange, and the recognition of the varying degrees of tolerance of the main agricultural crops to the soil-acidity complex, other methods for estimating lime requirements were developed, which measured the degree of soil unsaturation in terms of the amount of lime needed to bring the pH of a soil in the laboratory to a desired level.

The two methods more commonly used in advisory work in England and Wales for estimating the lime requirement of a soil are (*a*) a modification of the Smith and Coull buffer-curve technique (1932) which assesses the amount of lime needed to bring the pH of a soil to 6·5, and gives results in close agreement with the Hutchinson–McLennan method, and (*b*) the estimation of the exchangeable CaO including any free calcium carbonate if present in small amount. This latter method is used chiefly in Wales and has been developed by Rice Williams (private communication). The soil is leached with N/2 acetic acid and a figure of 0·30 per cent. exchangeable CaO (+small quantities of free $CaCO_3$) is taken as the general safety level above which no lime is recommended. For light-textured soils a lower limit is accepted, and for heavy-textured soils and organic soils a higher standard is used. In addition, the pH of the soil is determined in order to check any soil abnormalities such as may occur in glasshouse soils containing much calcium sulphate, and which may give a high figure of acetic-acid-soluble calcium at a low soil pH.

Both these methods of approach estimate fundamental soil properties which can be quite accurately measured in the laboratory. The difficulties arise when these laboratory estimates are used in advisory work to recommend applications of lime in the field, as the results have to be interpreted in the light of considerable field experience of the soil in

question and all the following factors need careful consideration when translating laboratory lime requirements to field lime requirements.

Field Factor

Methods for estimating lime requirements based on laboratory titration curves have shown, particularly in continental experiments (Christensen and Tovborg-Jensen, 1926; De Vries and Bruin, 1947), that the soil in the field needs two to three times as much lime to bring its pH to a given value as is found in the laboratory. The published data in this country and America (Mitchell, 1936; Whelan, 1939; Dunn, 1943; Heintze, 1949) indicate that similar factors are also necessary, although in some cases the field factor was 1·5 or less. It is perhaps unfortunate that in many of these investigations only changes in the pH of the soil or its calcium status were followed in the field, and they were not accompanied by properly designed liming experiments to assess the effect of different rates of lime on crop yields. It has been generally assumed that the 'ideal' pH of a soil to give freedom of cropping, minimize phosphate fixation, and confer other beneficial properties is 6·5, and undoubtedly in routine advisory work this is a very useful approach. The practice of selecting some 'ideal' pH for a given cropping system has been widely adopted, and consequently laboratory lime requirements have been estimated which will bring a soil to a selected pH, and a factor applied when making field recommendations. In aiming to bring the pH of the soil in the field to some selected value, the effect of differential dressings of lime on crop yields and other soil properties has often been overlooked. Even small quantities of lime may be adequate to depress the availability of toxic manganese and aluminium, and there is little doubt that actual calcium deficiency only operates at relatively low pH values.

The Evaluation and Effectiveness of Different Liming Materials

There is a wide range of materials which can be used for liming; burnt limes, hydrated lime, and ground limestone of varying degrees of fineness, of high calcium content, or with varying percentages of magnesium. In addition ground chalk, other natural liming materials, and waste limes of industrial origin may also be used. One difficulty in practice is to evaluate the different materials so that equivalent amounts in terms of neutralizing value are applied. In a recent paper (Smith, Corrie, and Simpson, 1951) a simple method for estimating the total neutralizing value of liming materials has been proposed, and it would appear that in general where this method has been used to calculate equivalent quantities of different materials the quantities have produced the same effect on the pH value of the soils to which they were applied. In other Scottish experiments (Reith and Williams, 1949) different liming materials applied on the basis of their total neutralizing value all effected considerable increases in crop yields, pH, and acetic-acid-soluble CaO. The differences between forms of lime were found to be unimportant except that blast-furnace slag and shell sand were slightly inferior, at least initially. Coarsely ground limestone appeared to be equally as effective as finely

ground limestones, and this finding is in general agreement with the results of other workers (Albrecht, 1946; Pierre, 1930; MacIntire *et al.*, 1933; Doak, 1941).

In the case of wet waste liming materials, there is probably some justification in recommending heavier applications than would be desirable merely from a consideration of equivalent quantities, owing to the difficulties of getting uniform distribution.

The Tolerance of Different Plant Species to Soil Acidity

American workers have published detailed lists of the approximate pH levels at which the main agricultural plants fail due to acidity. A similar list has been compiled for the main crops in England by W. M. Davies (1938). Some of the main difficulties in regarding these levels as absolute are due to seasonal variations in soil pH and the different behaviour of various soils. It is not uncommon for the pH of a soil under natural conditions to vary by as much as a whole pH unit, due to changes in salt concentration occasioned by bacterial activity, cropping, application of fertilizers, and changes in the soil-moisture content (Huberty and Haas, 1940). Crops will often grow satisfactorily on organic soils at low pH levels where they would certainly fail on mineral soils. There is clearly no one pH figure that will satisfy all crops and all conditions except one that will bring the lime status to a point where even the most susceptible crops are safe, and this more than satisfies the requirement for a crop such as potatoes. As it is usual in farming practice to lime for a full rotation and not just one crop, it is not only essential to know the rotation, but also to make allowances for loss of lime by leaching, especially if the last crop of a rotation happens to be a sensitive crop. The possibility of inducing micro-nutrient deficiencies such as manganese or boron by liming certain soils to a pH of 6·5 or more must also be borne in mind.

The Quality and Nutritive Value of the Crop

Quite apart from any effect lime may have on crop yields, it may affect the quality and nutritive value of the crop by influencing the calcium content or by other indirect effects such as increasing the clover percentage in a grass sward (Davies, 1941; Davies and Milton, 1945; Fagan *et al.*, 1945; Findlay, 1945; Laird, 1945; Milton and Davies, 1947). That lime may not immediately and invariably give crops with a higher content of calcium is evident from Reith and Williams's data (1949).

Soil Cultivations

It is generally assumed when making liming recommendations in the field that only the surface of the soil to a depth of 6 or 8 in. will be concerned. Whilst this practice may be satisfactory for normal ploughing, it is often necessary to modify it for deeper ploughing, not merely because a greater depth of soil is brought into cultivation, but also because the pH trends down many soil profiles show marked variations. It is not uncommon to find the surface 6 in. of a permanent grass field on a

soil derived from a calcareous parent material to be quite acid. Deep ploughing on such a field may supply all the lime necessary. Conversely many light-textured soils recently pressed into arable cultivation may have subsoils with much lower pH values than the surface soil, and liming recommendations when such soils are deep-ploughed must be given careful consideration.

In view of the many difficulties attendant on any attempt to interpret accurately laboratory estimates of lime requirement it is surprising how few field experiments have been carried out in Britain to compare the effects of different rates and types of liming materials on crop yields. Clearly, different laboratory methods can only be satisfactorily compared by testing them in such experiments, and it is the purpose of this paper to present data from various trials that will permit some evaluation of these methods and the interpretation of the results.

Experimental

Long-term liming experiment carried out at Harper Adams Agricultural College from 1928 to 1944

This experiment was a 4×4 Latin-square experiment (individual plot size $\frac{1}{4}$ acre) testing finely ground limestone at the rates of 0, 25, 50, and 100 cwt. per acre. The soil was a light loam, Newport Series, derived from glacial sand and freely drained. At the start of the experiment the pH of the soil was 4·7 and the lime requirement as determined by the Hutchinson–McLennan method was approximately 40 cwt. calcium carbonate per acre. No further dressings of lime were applied during the course of the experiment, and manurial treatments were normal for the crops grown and uniform over the experimental area. Determinations were made each year in the spring of the pH, exchangeable CaO, free $CaCO_3$, and the Hutchinson–McLennan lime requirement. The percentage CaO in the dry matter of the crops was determined occasionally.

Crop yields

Table 1 presents the mean yields for the various treatments over the period 1929–39; yield data for later years are not available.

Unfortunately, owing chiefly to the large plot size, soil variations were greater than usual, and the standard error per plot was rather large in most years. In every year, except when potatoes and oats were grown, the yields from the limed plots were significantly higher than those from the untreated plots, although with sugar beet in 1939 the difference between the nil treatment and the 25 cwt. per acre treatment was not significant. Over the eleven cropping years the differences between the 50-cwt. and 100-cwt. treatments were never significant. The yields from the 25-cwt. treatments were only significantly lower than those from the more heavily limed plots for barley, clover hay, and beet in 1932, 1933, and 1939 respectively. In the Tunstall liming experiment (Oldershaw and Garner, 1951), where dressings of ground chalk at 0, 1, 2, 3, and 4 tons per acre were compared on very light sand with an initial lime require-

TABLE I

Year	Crop	*Cwt.* $CaCO_3$ *per acre*				Mean yield	S.E.
		0	*25*	*50*	*100*		
1929	Barley: Grain	9·26	15·07	16·06	17·11	14·38	1·13
	Straw	9·54	13·58	14·12	16·40	13·41	0·806
1930	Sugar beet: Roots	4·05	9·09	10·25	10·09	8·37	0·599
	% Sugar	16·69	17·07	17·14	17·19	17·02	0·258
1931	Sugar beet: Roots	0·61	4·62	5·24	5·70	4·04	0·641
	% Sugar	16·35	16·78	17·03	17·41	16·89	0·223
1932	Barley: Grain	2·0	14·8	23·0	24·3	16·0	1·83
	Straw	0·7	15·0	19·7	21·1	14·1	1·47
1933	Clover	2·4	16·3	28·8	28·1	18·9	3·43
1934	Swedes	5·20	12·82	15·89	16·02	12·48	1·24
1935	Potatoes	9·54	10·03	10·18	10·92	10·17	0·479
1936	Oats: Grain	30·4	31·5	29·8	29·0	30·2	..
	Straw	34·7	34·9	37·9	38·8	36·6	..
1937	Clover	11·1	25·7	28·1	24·1	22·3	..
1938	Wheat: Grain	26·3	36·4	36·6	33·3	33·2	1·31
	Straw	30·0	42·2	41·8	41·4	38·9	1·04
1939	Sugar beet: Roots	1·04	2·53	5·83	7·81	4·30	0·682
	% Sugar	15·51	15·46	15·89	16·96	15·95	..

All yields for cereals (grain and straw) and clover crops are in cwt. dry matter per acre.

All yields for roots are in tons clean roots per acre.

ment of 17 cwt. per acre $CaCO_3$ by the Hutchinson–McLennan method, and 25 cwt. by a buffer-curve method, there were rarely any significant differences in yield between the three highest lime dressings for the first 9 or 10 years. Even the 1-ton dressing gave nearly 90 per cent. of the crop produced by the 4-ton dressing over the first 7 or 8 years. After this period of time, the loss of lime from the soil was beginning to make itself felt on the plots receiving the lowest dressings.

The first five crops at Harper Adams were all rather sensitive to acidity and provide a drastic comparison of the different liming rates. On the average, liming at 100 cwt. $CaCO_3$ per acre or $2\frac{1}{2}$ times the laboratory lime requirement gave approximately 5 per cent. higher yields than the 50-cwt. dressing. With the introduction of less sensitive crops the differences were not so marked and in some cases slightly in favour of the lower liming rate. The beet crop grown 11 years after liming showed marked benefits from the heavier liming rates. Over the 11 years, in which a higher proportion of sensitive crops was grown than in an average farm rotation, the 50-cwt. dressing gave 98 per cent. of the yield of dry matter given by the 100-cwt. dressing, the 25-cwt. dressing gave 81 per cent., and the no-lime plots gave 30 per cent.

Changes in pH

Fig. 1 shows the pH changes during the period 1928–44 (each figure is the mean of four plots).

The highest pH reached by the soils was some 4 or 5 years after application of the lime. In the case of the 50-cwt. dressing the highest pH reached was 6·1, and if lime had been used at the lime-requirement

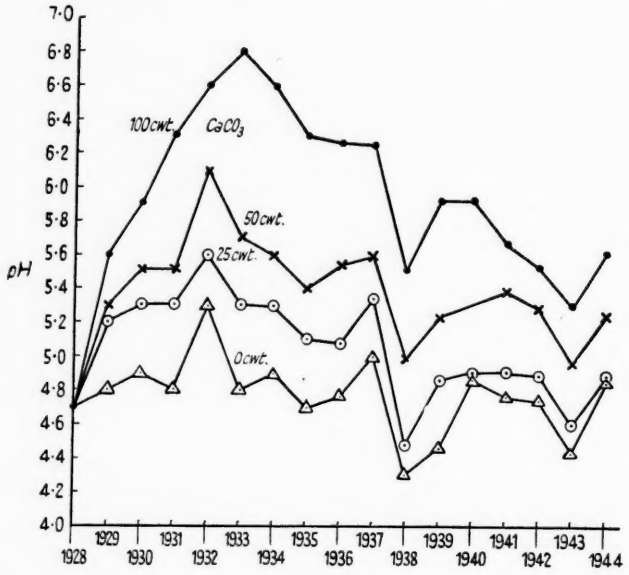

FIG. 1.

rate of 40 cwt. $CaCO_3$ per acre, the highest pH would probably have been 5·8–6·0. Even after 16 years there were still small apparent differences in pH between the nil and the 25-cwt. dressings. If any attempt were made to assess the lime requirement from methods involving pH determinations, then in the year or two following the liming, when the pH of the 100-cwt. plots was still only 5·6–5·9, further liming might have been recommended. After 4 or 5 years the assessment of the lime requirement from pH determinations would have been fairly reliable. This lag of 4–5 years in reaching the maximum pH did not occur at Tunstall (Heintze, 1949) except in the case of the four-ton dressing, but Smith *et al.* (1951) found that some 18–30 months were necessary for the full effects of liming to be reflected in pH changes in their experiments.

Seasonal effects were marked in 1932, 1938, and 1943, and affected all treatments in a similar way. The marked rise in pH in 1932 probably reflects delayed nitrification, whereas the falls in 1938 and 1943 may have been due to enhanced nitrification and/or drier conditions.

Changes in lime requirement—Hutchinson–McLennan method

Fig. 2 shows the changes in lime requirement as determined by the Hutchinson–McLennan method, expressed as per cent. CaO.

As in the case of the pH values, the time needed for the maximum effect of lime in reducing the estimated lime requirement was 4 or 5 years; indeed, the requirement after 2 years, even on the most heavily

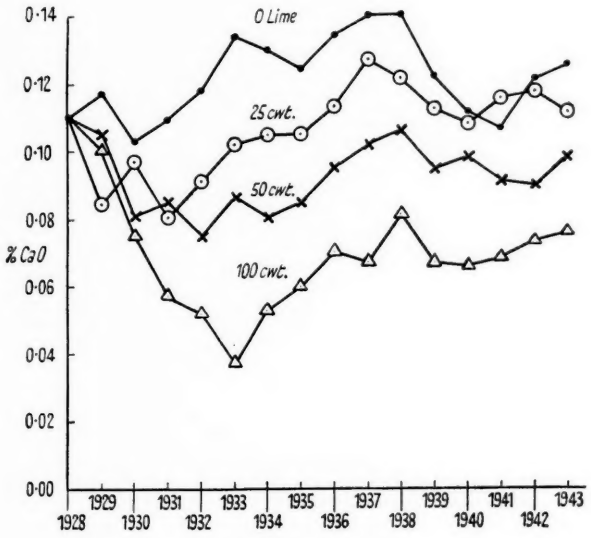

FIG. 2.

dressed plots, was still 0·7 ton CaO per acre compared with the initial requirement of 1·1 tons, and the minimum lime requirement recorded for this dressing was 0·4 ton CaO. Quite clearly the Hutchinson–McLennan method is not a better guide than pH determinations in assessing the lime requirement of a soil in the years immediately following lime applications.

Changes in exchangeable CaO

The per cent. exchangeable CaO during the period is plotted in Fig. 3. As with the previous determinations, a few years elapsed before the maximum changes were recorded, and thereafter there was a gradual decline in exchangeable calcium in all the treated plots. Lime requirements based on determination of exchangeable calcium would not be reliable during the first few years after lime applications, but thereafter, with establishment of proper standards, they would be quite satisfactory.

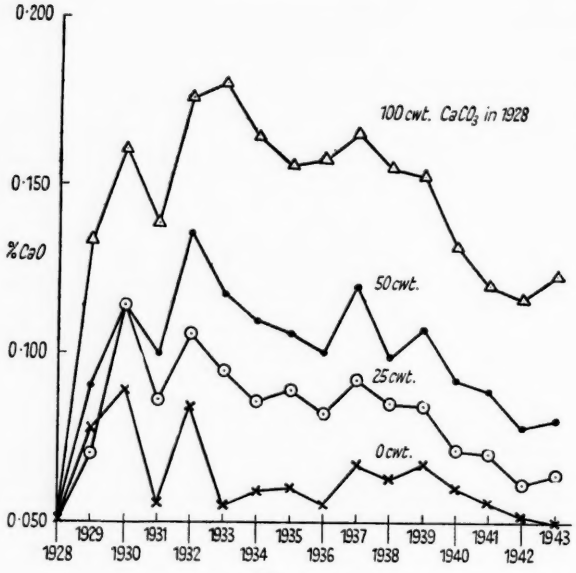
0·200
0·150
%CaO
0·100
0·050
100 cwt. CaCO3 in 1928
50 cwt.
25 cwt.
0 cwt.
1928
1929
1930
1931
1932
1933
1934
1935
1936
1937
1938
1939
1940
1941
1942
1943

FIG. 3.

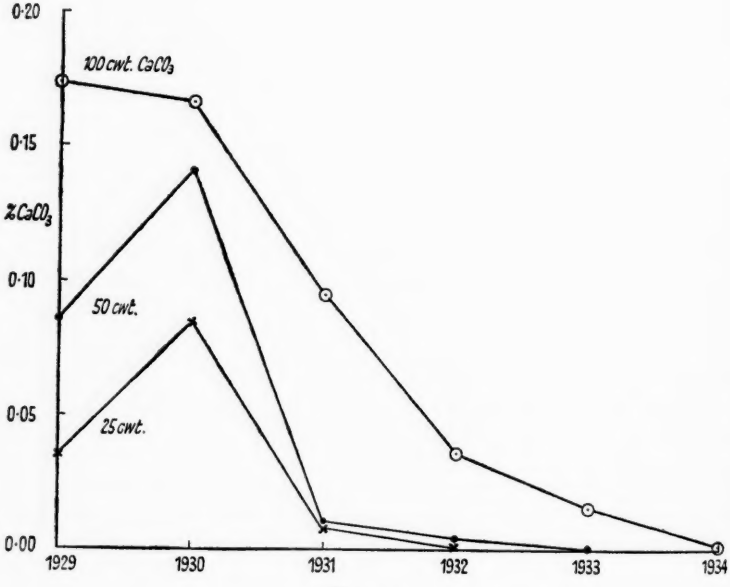
0·20
0·15
%CaCO3
0·10
0·05
0·00
100 cwt. CaCO3
50 cwt.
25 cwt.
1929
1930
1931
1932
1933
1934

FIG. 4.

Changes in per cent. free $CaCO_3$, and per cent. exchangeable CaO+free $CaCO_3$ expressed as CaO

Free calcium carbonate persisted on the most heavily dressed plots for 5 or 6 years, and for 3–4 years on the other plots (Fig. 4). To some extent this would account for the delayed effects observed on the pH, exchangeable CaO, and lime requirement as determined by the Hutchinson–McLennan method.

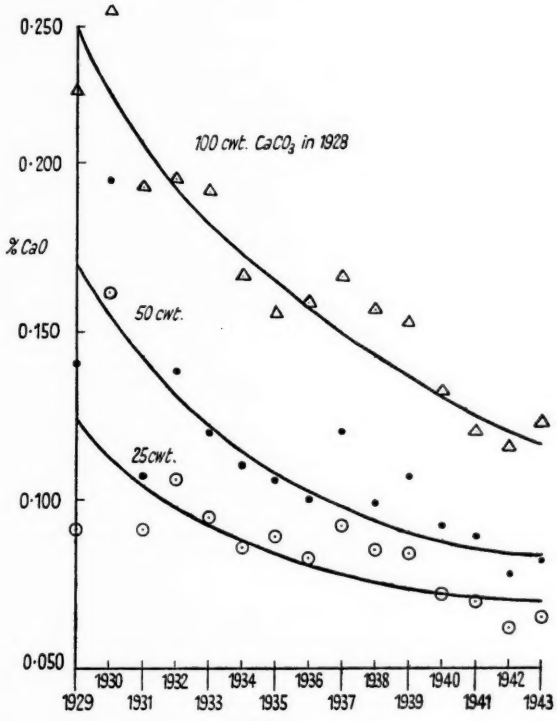

FIG. 5.

Fig. 5 shows the gradual reduction in the per cent. CaO present in the soils as exchangeable calcium and free calcium carbonate. The soil at the beginning of the experiment in 1928 contained 0·05 per cent. exchangeable CaO, and the theoretical amount of exchangeable CaO+free $CaCO_3$ immediately after application would have been 0·33 per cent., 0·19 per cent., and 0·12 per cent. CaO for the 100-cwt., 50-cwt., and 25-cwt. dressings respectively. The actual amounts found in 1929 are lower than these figures, and they must reflect to some extent the losses of lime from the surface layers during the first year. Sampling errors, of course, would be expected to influence the results. There is clearly a gradual

loss of lime throughout the period of the experiment, the losses being greater in the early years and for the heavier dressings.

Given a satisfactory sampling technique, the estimation of exchangeable calcium + free calcium carbonate clearly gives the most satisfactory picture of the actual calcium status in the soil; as might be expected it reflects immediately the application of lime and there is a gradual fall in concentration with time.

It is possible from these curves to make an approximate estimate of the losses of lime from the surface soil at the various liming rates.

Approximate Loss of $CaCO_3$ (cwt. per acre per year)

	100-cwt. dressing	*50-cwt.*	*25-cwt.*
First 5 years . .	8	5	3
Second 5 years. .	4	2½	1½
Third 5 years . .	2	1	½
Total for 15 years .	70	42	25

Effect of liming on the calcium content of the crops

In addition to the loss of lime by leaching, the bigger crops grown after the application of lime will also remove more lime from the soil, unless compensated by a reduction in the calcium content of the crops, and it is of interest to examine the effect of lime on the calcium content. Nutritional aspects may also be important. Unfortunately the data are available for only a few years (Table 2).

TABLE 2

Per cent. CaO *in Dry Matter*

Original dressing of $CaCO_3$ *in cwt. per acre*	*0*	*25*	*50*	*100*
1930 Sugar beet: Roots .	0·244	0·235	0·256	0·275
Tops. .	1·213	1·300	1·448	1·376
1931 Sugar beet: Roots .	0·318	0·282	0·307	0·342
Tops. .	1·200	1·587	1·761	1·630
1932 Barley: Grain . .	0·074	0·067	0·057	0·057
Straw . .	0·296	0·372	0·352	0·409
1933 Clover hay . . .	2·19	2·06	2·15	2·47
1934 Swedes: Roots . .	0·353	0·365	0·451	0·473
Tops . .	1·484	1·702	2·095	3·059

The most marked effect was on the swede tops, where the heaviest dressing of lime doubled the calcium content, in addition to giving three times the yield of roots and probably a proportionate increase in the yield of tops. The effect on the roots was less marked but still pronounced. The calcium content of the sugar-beet roots was not greatly influenced except perhaps for the highest dressing, but the calcium con-

tent of the beet tops was generally higher where lime was applied. With barley, the calcium content of the straw, only, increased with liming, and the calcium content of the grain appeared to fall. In the case of the clover hay, only the heaviest dressing of lime increased the calcium content. At approximately half the lime-requirement rate (25 cwt.) the crops sometimes contained less calcium than the control crops, a point also recently noted by Chambers and Gardner (1951).

Liming experiments carried out by Advisory Chemists

In 1944 a series of liming experiments was initiated by the Liming Committee of the Advisory Chemists' Conference, some results of which have recently been published (Crowther and Walker, 1952).

One of the main objects of these experiments was to compare different liming materials when used at lime-requirement rates estimated by the Hutchinson–McLennan or similar methods. Some of them were similar to the experiments carried out by Reith and Williams (1949) in Scotland. In each experiment a standard liming material (actually ground burnt lime) was used at nil, half, and full lime-requirement rates, so that from the response curve thus obtained it would be possible to compare accurately the various liming materials. A large number of experiments was carried out and only some of the results relevant to the subject of this paper will be discussed.

Changes in pH effected by different liming materials, and comparison with crop yields

(*a*) *Comparison of ground limestones of definite fractions.* In these experiments three ground limestones of the following fractions were compared: (1) all falling between the 20–40-mesh sieves, (2) all falling between the 40–100-mesh sieves, and (3) all passing the 100-mesh sieve. There were eight replicated experiments, and over the period of 4 years for which data are presented in Table 3 thirty experimental crops were grown. The

TABLE 3

Changes in pH and Crop Yields (1944–7)

Centre	*No lime*	½ CaO	1 CaO	$CaCO_3$ *at full rate*		
				20–40 mesh	*40–100 mesh*	*100 mesh*
Bowness	4·6	5·1	5·5	5·4	5·7	6·0
Harewood	4·6	5·1	5·5	5·5	5·6	5·7
Blagdon	4·9	5·1	5·4	5·3	5·4	5·4
Moreton-Hampstead	4·5	5·4	6·1	5·7	6·0	6·2
Beaumaris	5·1	5·5	6·0	5·9	5·9	6·3
Filby	5·9	6·1	6·2	6·5	6·5	6·6
Cefnllidiart	5·2	5·7	5·9	5·9	6·0	6·2
Pencefn	5·0	5·4	5·6	5·7	5·8	6·2
Mean	5·0	5·4	5·8	5·7	5·8	6·1
Yields or scores as per cent. general mean for 30 crops	57·6	103·1	109·2	106·9	110·2	112·7

experiments compared no lime, ground burnt lime at half and full lime-requirement rates, and the three distinct fractions of ground limestone at the full rates. Each pH figure is the mean of all the replicates determined at 3- to 6-monthly intervals over the period of the experiments. The yields (or scores, where it was not possible to harvest the crop) are expressed as the per cent. of the general mean and are the averages from all the experiments.

These results indicate that the finest fraction of limestone effected the biggest rise in pH, and that ground burnt lime was little more effective than the coarser limestone fractions. The yield data are closely related to the pH changes, and lime at half-rate was not much inferior to the various liming materials applied at the full rate. Apart from the very fine limestone the other fractions and the burnt lime raised the average pH to 5·8 for the full lime-requirement rate, a result in close agreement with the Harper Adams experiment.

As far as possible acid-sensitive crops were grown in these experiments, but this was not always so; in any case, however, a bigger proportion of sensitive crops was grown than in an average rotation. In the case of the half and full lime-requirement dressings, it is clear that, even at these rates, the flat part of the response curve had been reached, but this does not mean that even higher dressings of lime would not have given some extra slight increase in yield.

(*b*) *Comparison of commercial ground limestones of varying degrees of fineness.* The results of four experiments are presented in Table 4, and the pH figures again are the means of replicate plots at 3- to 6-monthly periods from 1945 to 1947. The limestone with 50–55 per cent. passing the 100-mesh sieve is perhaps nearest to the average commercial grade in Great Britain.

TABLE 4

Changes in pH and Crop Yields (1945–7)

Centre	*No lime*	CaO ½ *L.R.*	CaO 1 *L.R.*	$CaCO_3$ 1 *L.R.*—% *passing 100 mesh*			
				20–25%	*30–40%*	*50–55%*	*100%*
Sutton-on-Forest	5·1	5·3	5·6	5·6	5·6	5·9	5·9
Llecheiddor .	4·8	5·1	5·4	5·3	5·3	5·3	5·7
Llethmeirch .	4·5	5·0	5·3	5·2	5·1	5·2	6·0
Prignant . .	4·7	5·1	5·2	5·1	5·1	5·3	5·8
Mean pH values	4·8	5·1	5·4	5·3	5·3	5·4	5·9
Yields or scores as % general means for 7 crops .	65·7	99·2	106·0	105·5	105·7	107·0	110·3

As in the previous series of experiments, the very fine limestone had the biggest effect on both yield and pH, and the coarse ground limestones were slightly inferior to the fine limestone, but apparently as good as ground burnt lime. Ground burnt lime at half the lime-requirement rate again gave yields not greatly less than lime at the full rate.

Other experiments compared waste limes, magnesian limes, and other liming materials of different geological origin. The general conclusions were that when applied at equivalent rates in terms of neutralizing value there was little to choose between them, although there was evidence that the finely ground limestones may be even better than ground burnt lime, and the coarse limestones may be slightly inferior.

Discussion

Most of the factors which need to be considered when interpreting laboratory determinations of the lime requirement of a soil have already been enumerated. The results from the Harper Adams and other liming experiments provide data for a critical examination of the various laboratory methods used in Britain, and of the conversion of these laboratory lime requirements into field requirements.

In the Harper Adams experiment ground carbonate of lime was applied at 0, 25, 50, and 100 cwt. per acre; the Hutchinson–McLennan lime requirement was 22 cwt. CaO per acre, and the lime was applied therefore at approximately nil, half, full, and twice the laboratory determination. In the early years of the experiment the half lime-requirement rate gave yields only slightly less than the heavier rates on acid-sensitive crops such as beet and barley. Differences in yield between the two higher liming rates were small and not significant. In the other experiments quoted lime was applied at nil, half, and the full lime-requirement rates as determined by the Hutchinson–McLennan method, and the half rate in these experiments also gave yields only some 10 per cent. less than the full rate. In the early years of the Tunstall experiment (Oldershaw and Garner, 1949) liming at rates heavier than the Hutchinson–McLennan requirement gave only slightly higher yields, and the differences between the higher rates were very small indeed. The 1939 crop of beet at Harper Adams showed a very definite advantage for the double rate, and in the later years at Tunstall the lower liming rates gave definitely smaller yields than the heavier rates.

It would appear from these results, certainly in the 3 or 4 years following the application of lime, that only small differences in yield are obtained from application at half, full, and higher rates of the Hutchinson–McLennan requirement. Lime at half rates effects big increases in yields, and there is a general tendency for the heavier rates to give still further slight increases in yield on the acid-sensitive crops grown in these experiments. Clearly the flat part of the response curve is reached by liming at half rate, and there must be a fairly wide liming rate from half to double or even greater rates, for which the benefits from heavier liming are only slight. When considering the possibility that liming at double or more the lime-requirement rate may induce micro-nutrient deficiencies on some soils, the usual farming practice of liming at intervals of 4 or 5 years, and the bigger proportion of more acid-tolerant crops grown on most farms than in these experiments, there can be few cases where liming at greater than the Hutchinson–McLennan rate will be necessary or profitable. In the drier parts of the country, and where

acid-sensitive crops may form a bigger proportion of the rotation, there may be instances where higher rates of liming will be advantageous.

The one difficulty would appear to be in estimating the lime requirement of a soil in the first year or two following application of lime. Until applied lime has been entirely absorbed as exchangeable calcium, the Hutchinson–McLennan method may overestimate the requirement, as indeed would methods based on the determination of exchangeable calcium. The reason for this is due to applied lime not being immediately converted into the exchangeable state.

These and other experiments indicate a time-lag of 12 to 30 months or more in the case of the usual liming materials, and this is reflected in the soil pH and exchangeable calcium, which in the Harper Adams experiment did not reach their maximum level, particularly at the higher liming rates, for 3 or more years. Methods, therefore, which do not take into account the slowly soluble residues of recent lime applications are likely to overestimate the actual lime requirement of the soil. This will apply to the Hutchinson–McLennan method, methods based on the determination of exchangeable calcium, and methods using the titration-curve technique where the pH changes in a soil are followed by shaking with solutions of varying strength of calcium hydroxide. Once all the calcium applied has been converted to exchangeable calcium, any of these methods by the adoption of suitable standards could be used to estimate the field lime requirement of a soil. Where lime is applied at the rates found by the Hutchinson–McLennan or similar methods, the pH of the soil in the field will seldom be brought to 6·5, but this would not appear to matter greatly. Such applications seem normally to bring the pH to 5·8 or thereabouts, but whatever the effect on pH, the crop yields are only slightly less, if at all, than those obtained from heavier dressings.

In the case of recently limed soils (and these are rather numerous in advisory work) the best method for assessing the lime requirement would appear to be the estimation of exchangeable calcium and free carbonate, as actually used in Wales by Rice-Williams (private communication). Even so, there are one or two practical difficulties of sampling which may sometimes interfere, namely, where recent applications of ground limestone have been made on grassland, and on soils to which burnt lump lime has been applied, a proportion of which has not reacted but remains in the soil in lumps owing to poor slaking. In the first case, the trouble arises because the usual type of spiral auger does not pick up all the limestone on the surface of the grass sward, and in the second case because, whilst it is easy to pick out large lumps of lime before grinding the soil for analysis, it is quite impossible to get it all out.

However, apart from the difficulties on recently limed fields, it is clear that any of the methods used in estimating the lime requirements of soils should be sufficient to enable economic rates of liming to be determined. In rotations not including any of the very acid-sensitive crops, lime at half or the full rates found by the Hutchinson–McLennan or similar methods may be expected to give as good results as heavier dressings. Where freedom of cropping is essential, and in the drier parts of the country, there may be a case for recommending lime dressings greater

than the laboratory figure. The relatively slight advantages of heavier dressings may be due to the better chance of getting more even distribution, beneficial effects on soil structure, enhanced nitrification, and the quicker neutralizing of subsoil acidity due to greater removal of lime from the surface by leaching. There is certainly no case for a universal use of a field factor for converting laboratory lime-requirement estimations to field requirements.

With a given rotation, a knowledge of the soil type and history of recent liming practices, and bearing in mind all the factors discussed in this paper, there is little doubt that the interpretation of laboratory lime requirements, determined by a variety of methods, can be put on a very sound basis. The few results quoted from the Advisory Chemists' experiments and in Reith and Williams's paper (1949) indicate that the usual commercial ground limestone (50–55 per cent. passing the 100-mesh sieve) gives the same results as equivalent quantities of ground burnt lime, coarser limestones may be slightly inferior, and finer limestones a little better. Most other forms of liming materials which can be evenly applied are as effective as equivalent quantities of burnt lime or ground limestone. As long as lime is applied at rates approximating to the quantities found by the Hutchinson–McLennan or similar methods, its form and exact amount are not of paramount importance, and only careful consideration of all the various factors concerned can justify a radical departure from this practice.

Summary

Soil and yield data from a long-term liming experiment at Harper Adams Agricultural College have been presented. Lime applied at approximately half, full, and double the Hutchinson–McLennan lime-requirement estimate had very similar effects on the yields of acid-sensitive crops in the early years of the experiment. The subsequent changes in pH, exchangeable calcium, and the Hutchinson–McLennan lime requirements indicated a 2- or 3-years' delay in applied lime having its maximum effect on these soil values, although effects on crop yields were immediate. The anomalous results often found in practice, where recently limed soils still show marked lime requirements, may be explained by this delay. Until lime applications have been absorbed into the soil complex, it is therefore suggested that the best method for assessing the lime requirement is the determination of the exchangeable calcium and free calcium carbonate if present in small amounts, although such a method depends upon the establishment of satisfactory local standards for different soil types. Other experiments carried out by Advisory Chemists also indicate that liming at half and full Hutchinson–McLennan rates gives yields only 10–15 per cent. higher for the heavier dressings. Over a fairly wide range of liming, therefore, yields may be markedly improved, and with a knowledge of all the various factors involved, almost any method used for estimating lime requirements can be adopted if recently limed soils are excluded. The few data presented from the experiments involving the use of different ground limestones

indicate little difference between the various forms, with some slight advantage for finer grinding.

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REFERENCES

ALBRECHT, W. A. 1946. Soil Sci. **61,** 265.
CHAMBERS, W. E., and GARDNER, H. W. 1951. J. Soil Sci. **2,** 246.
CHRISTENSEN, H. R., and TOVBORG-JENSEN, S. 1926. A. Trans. 2nd Comm. Int. Soc. Soil Sci. Groningen, p. 94.
CROWTHER, E. M., and WALKER, T. W. 1952. Agriculture (in the press).
DAVIES, W. M. 1938. Agric. Prog. **15,** 111.
DAVIES, R. O. 1941. J. Ecol. **29,** 49.
—— and MILTON, W. E. J. 1945. Welsh J. Agric. **18,** 43.
—— —— 1945. Emp. J. Expt. Agric. **13,** 184.
DE VRIES, O., and BRUIN, P. 1947. Emp. J. Expt. Agric. **15,** 260.
DOAK, B. W. 1941. N.Z. J. Sci. Tech. **23A,** 24.
DUNN, L. E. 1943. Soil Sci. **56,** 341.
FAGAN, T. W., JONES, E., WILLIAMS, E. E., *et al.*, 1945. Welsh J. Agric. **18,** 73.
FINDLAY, W. M. 1945. Scot. J. Agric. **25,** No. 3, 171.
HALL, A. D. 1905. Fertilizers and Manures, p. 253.
HEINTZE, S. G. 1949. J. Roy. Agric. Soc. England, **110,** 98.
HUBERTY, M. R., and HAAS, A. R. C. 1940. Soil Sci. **49,** 455.
LAIRD, R. 1945. Scot. J. Agric. **25,** 98.
MACINTIRE, W. H., *et al.* 1933. J. Amer. Soc. Agron. **25,** 285.
MILTON, W. E. J., and DAVIES, R. O. 1947. J. Ecol. **35,** 65.
MITCHELL, R. L. 1936. J. Agric. Sci. **26,** 664.
OLDERSHAW, A. W., and GARNER, H. V. 1949. J. Roy. Agric. Soc. England, **110,** 89.
PIERRE, W. H. 1930. Soil Sci. **29,** 137.
REITH, J. W. S., and WILLIAMS, E. G. 1949. Emp. J. Expt. Agric. **17,** 265.
RICE WILLIAMS. Private communication.
SMITH, A. M., CORRIE, A., and SIMPSON, K. 1951. The Analyst, **76,** 58.
—— and COULL, R. 1932. Soil Res. **3,** 10.
WHELAN, L. A. 1939. J. Agric. Sci. **29,** 306.

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SOME MORPHOLOGICAL FEATURES ASSOCIATED WITH POOR SOIL DRAINAGE

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WITH TWO PLATES

IT has been shown by several workers (Ellis, 1932; Milne, 1935; Bushnell, 1942, 1944, 1948; Glentworth and Dion, 1949) that soils showing various degrees of hydromorphism form an important part of the soil catenas occurring in many parts of the world. The larger part of the British Isles is covered by soils displaying evidence of gleying. They are particularly extensive in the north and west where the heavier rainfall tends to cause seasonal waterlogging even on normal relief.

For the purpose of this paper the term 'gley' will be used to describe the pale grey or blue-grey soil colours, often with associated rusty or ochreous mottling, which are believed to result from permanent or seasonal waterlogging; and 'gley soils' will include profiles in which such features occur, although it is recognized that where gleying plays a minor part the soil might be more properly described as a slightly gleyed form of some other major group.

The profiles of gley soils are influenced by many factors besides the degree of wetness (Clarke, 1941); differences in climate, parent material, vegetation, and degree of maturity produce modifications which lead to a bewildering variety of profile morphology. Differences in profile texture, especially, are responsible for variations which will be discussed later in this paper, but it seems possible that a relatively small number of basic patterns, often incompletely expressed, may be detected in the majority of hydromorphic soils.

The essential features seem to be well represented in soils with a perched seasonal water-table, such as occur widely, for instance, on glacial till in the north-west of England. Here, at altitudes below about 500 ft. O.D., the annual rainfall is about 30 to 40 in., fairly well distributed over the year except for a well-marked minimum from March to June. Temperatures range from about 40° F. in January to about 60° F. in July. The natural vegetation was probably wet woodland (oak, alder, &c.) interspersed with wet meadows (*Juncus*, *Carex*, *Deschampsia*, &c.) (Davies and Owen, 1934). Many centuries of farming, however, have left few if any virgin sites, and the descriptions below have been taken from fields under permanent pasture.

The normal catenary sequence of soils on gently undulating topography with slopes of about 4° usually shows Brown Earths on the higher ground, with increasing intensity of gleying down the slope to peaty gley soils and peat in the lowest sites (Fig. 1) (cf. Glentworth and Dion, 1949). There are many exceptions to this sequence, however; level sites, even where relatively high, are usually occupied by strongly gleyed soils, whilst local variations in texture of the parent material often lead to local flush effects causing patches of very poor drainage even in generally better drained areas.

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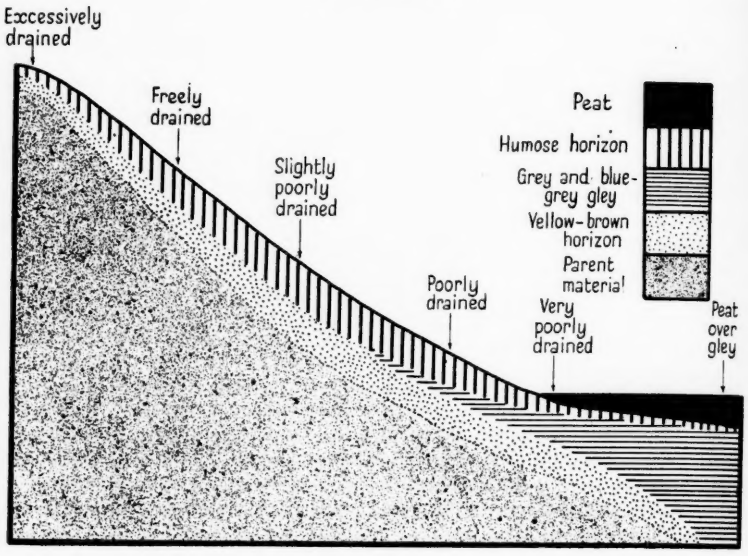

FIG. 1. Drainage catena in north-west England.

Poorly drained profile (Fig. 2)

A typical poorly drained profile on sandy clay or clay loam till shows about 4 in. of fairly dark brownish-grey surface soil with a crumb to soft granular structure and dominated by grass roots. Rusty mottling along the root channels sometimes occurs in this horizon but is usually more marked in the layer below, which may be about 6 in. thick, is dull grey, and has a small cloddy or nutty structure. Rusty mottling along the root channels is often very pronounced in this horizon, and in certain instances soft concretions occur. Occasionally the deposit of ferric oxide as concretions and as a surface coating on pebbles and structural aggregates may be so intense as to form a cemented layer known locally in Wales as 'suntur' and in Cumberland as 'roche'. The next horizon, perhaps 6 in. in thickness, is pale grey or bluish-grey, sometimes with irregular yellow spotting particularly at the base. A weak prismatic structure may be discernible, but more commonly this horizon appears almost structureless. The next horizon, which varies greatly in depth, shows a pronounced prismatic structure with pale grey or bluish-grey colours along all the structure faces and root channels, and bright yellow or orange colours within the structural elements. Patches of black manganese dioxide staining are a common but not invariable feature of this horizon. Both the amount and mode of occurrence of manganese dioxide in gley soils seem to be very erratic; in some profiles very small concretions are dotted throughout, in others quite large irregular cementations are very abundant in the pale grey horizon, whereas in others again only a staining on the structure faces occurs in the lower

horizons. The greater part of the writer's experience, however, has been with acid soils in which the above forms have been observed, but it seems likely that depositions of manganese dioxide are more common in soils with a neutral or alkaline reaction, at least in the subsoil.

The yellow and pale grey mottled horizon merges gradually into the parent material which, in the case of heavy glacial till, often has large prismatic structure to great depth, with bluish-grey colours on all the structure faces. Especially in the upper part of this lowest horizon a narrow zone of yellow-brown or orange-brown colour often occurs between the grey film on the structure face and the parent material colour within the mass.

In the above description the root channels are shown as having a rusty coating in the upper horizons and a grey or bluish-grey one in the lower part of the profile. Similarly, when stones from the upper horizon are broken they often show rusty or brown colours near the surface (of the stones); in the grey gley horizon they may be grey or greenish-grey even to the centre, whereas in the lowest part of the profile they usually show a narrow grey layer at the surface, inside which a yellow-brown or orange-brown zone merges gradually into the natural rock colour towards the centre.

The profile described above, which seems to correspond to the 'poorly drained' members of the 'Association' of Glentworth and Dion (1949), appears to form the most complete expression of a profile pattern common to a great number of gleyed soils.

Slightly poorly drained profile (Fig. 3)

In soils with somewhat better drainage, the 'slightly poorly drained' members of Glentworth and Dion, a similar general pattern can be discerned; the rusty mottling is less marked but is usually present near the surface, and the pale grey mottling is present on root channels and structure faces in the lowest layers. The pale grey gley horizon is very poorly developed or completely absent, the yellow-brown colour typical of the freely drained Brown Earth profile being more apparent in the subsoil.

Very poorly drained profile (Fig. 4)

In soils with poorer drainage, the 'very poorly drained' profiles, the grey gley horizon is very greatly enlarged and dominates the morphology of the subsoil. In some profiles, perhaps where there is an occasional supply of oxygen from below or where artificial drainage has been effected, bright yellow-brown, orange, or rusty mottling occurs along dead root channels, being so intense in some cases as to form hard tubes around the old root tracks (cf. Balls, 1951). Living roots appear always to produce a pale grey channel, although in some cases they follow the yellow-brown tube of an old root course, but even there a narrow pale grey zone can usually be detected immediately adjacent to the live root. It seems probable that this orange or rusty mottling in the lower horizons, which, in some cases at least, seems to consist of lepidocrocite (Muir and Brown 1951), is associated with profiles having the peaty surface typical of these very poorly drained soils.

Variations due to differences in texture and structure

The profile patterns described above seem to be general in soils formed on a wide variety of parent materials, but variations of many kinds occur. The heaviest parent materials, such as clays and silty clays, show profiles essentially similar to those on medium textured till (Fig. 5). As a rule, however, they are much shallower and the mottling is much finer, the pale grey colouring along the root channels and on the structure faces being often only a fraction of a millimetre thick. But the rule is not without exceptions, and more coarsely mottled patterns occur even in very heavy textures. The impermeability of the very heavy soils causes water to perch much nearer the surface so that the main grey horizon occurs immediately below the surface root mat. More roots than usual penetrate the grey horizon, and rusty mottling is fairly common.

The level at which water perches in gley soils appears to depend on several factors. Gleying in sandy profiles usually results from the presence of a relatively impermeable layer within or not far below the solum. In many medium-textured soils a somewhat heavier-textured horizon occurs under the grey layer and presumably retards or impedes percolation, although there is some slight evidence to suggest that in the first place this texture difference may sometimes be an effect rather than a cause of gleying.[1] In many profiles, however, little texture variation occurs, and it seems likely that the more intense gleying in the upper horizons is partly the result of the smaller structural elements which increase the moisture capacity (Nicholson, 1935) and bring a much larger proportion of soil material into contact with the reducing agents. The smaller structural elements in the upper horizons probably result largely from root action, which may partly account for the observation in Lancashire that, on comparable parent materials, the grey gley horizon seems to be relatively higher in the profile in the moorland foot-hills, where somewhat shallow-rooted grasses and sedges have probably been dominant in the natural vegetation, and deeper on the lower ground where the deeper-rooting deciduous trees were widespread (cf. Ototski, quoted by Glinka, 1927; Lachaussée, 1950).

Sandy profiles rarely show the pale grey mottling on the background of the parent material colour described for the C horizon of heavier soils, although where the water-table is held up by clay below the sand such features occur in the clay. The sand offers no large structure faces as channels for moisture movement, and, being very permeable, every particle is open to the influence of reducing agents in the waterlogged layer. Old root channels, however, serve as nuclei for ferric oxide deposition, and in some sandy soils the tendency for iron concretions and cementation to occur is very strong.

[1] There is little doubt that gleying increases the rate of weathering, but whether this leads to a lighter or heavier texture depends on several factors. Greater weathering may lead to a heavier texture in the first place by the production of a greater proportion of fine particles. If, however, eluviation is possible and is more rapid than weathering, the gley horizon may be lighter even from the beginning. Eventually, destruction of weatherable minerals must lead to a lighter texture.

Profiles with a deeper water-table (Fig. 6)

In some soils a water-table, often a regional ground-water table, occurs in or below the C horizon. If the profile is permeable, either because of light texture or well-developed structure, the surface horizons will show the features of the normal freely drained soil, and only the mottling on the structure faces and root channels in the C horizon and the grey layer below it will reveal the influence of a water-table.

In a heavy or more coarsely structural profile, however, a different pattern often occurs, the key to which appears to lie in the structural features. In the zone of almost permanent waterlogging, say at 4 ft. below the surface, structures are difficult to observe but are almost certainly weakly developed. Above this, however, and often extending to the surface, strong prismatic structures develop due to expansion and shrinkage through the seasonal wetting and drying of a material rich in colloids. In the immediate surface horizons, granular or fine cloddy structures occur, although larger prismatic elements also appear during dry seasons. The colour pattern in such a profile shows pale or bluish-grey colours, often strongly rust mottled and spotted with small concretions, immediately beneath the surface vegetation mat. Below this, often at a depth of only a few inches in the heaviest soils, the prismatic structural elements have the pale grey surfaces and root channels, passing, sometimes through yellow-brown, to the natural parent material colour inside the element. As the water-table is approached the grey on the structure faces penetrates farther inside the elements until it becomes the dominant colour.

The explanation of the dynamics of the profile appears to be that the prismatic elements shrink during dry weather, and showers of rain are either absorbed in the surface horizons or travel down the cracks to feed the water-table below. During longer wet periods, however, the cracks fill up and the elements expand so that a large amount of water stands in the surface, forming a seasonal water-table in the immediate sub-surface horizons, and so reproducing in miniature the features described for the perched water-table profiles.

Where circumstances, such as a deeper or more receptive water-table, are such that water rarely stands on the surface, the surface horizons may show little sign of gleying, and the soils may then be classed as freely or only slightly poorly drained. On the other hand, the water-table may approach so near to the surface as to give almost permanent wetness with the consequent development of peat.

Gleying under a peat-forming climate

At altitudes of more than 1,000 ft. in north-west England and over much of west Scotland the wet and cool climate tends to promote the formation of peat, even on well-drained sites (Fraser, 1933; Pearsall, 1950). In those parts of Lancashire in which the soil patterns described below have been studied by the writer, the rainfall averages from 50 to 55 in. per annum, with a minimum in the spring months and a sharp rise during July and August. Average temperatures are about 34° F. in

January and 54° F. in July. The tendency towards peat formation is particularly strong on acid parent materials, and on the Coal Measures Sandstones and local glacial till a catenary sequence of soils shows gley features very different from those described in the earlier part of this

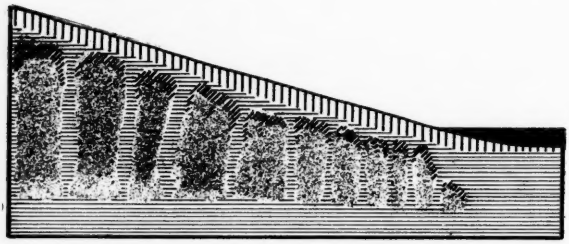

FIG. 6. Heavy-textured soils with permanent ground-water table. (Vertical scale much exaggerated.)

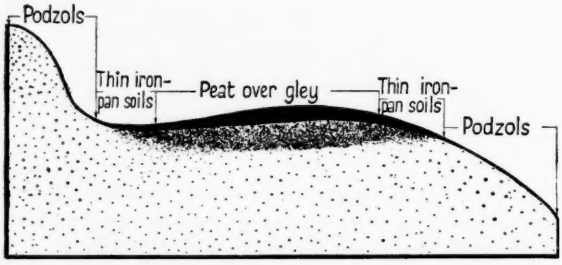

FIG. 7. Relationship of podzols, thin iron-pan soils, and peaty-gley soils to topography and depth of till.

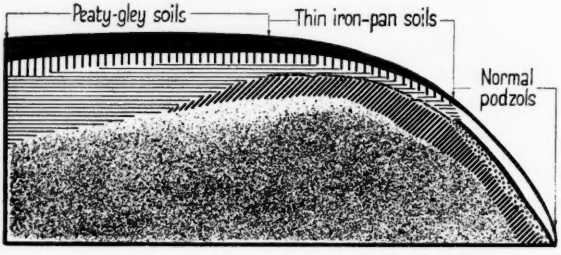

FIG. 8. Horizon relationships in podzols, thin iron-pan soils, and peaty-gley soils.

paper. The landscape is dominated by a series of steep scarps and very gentle dip-slopes forming a series of small plateau steps. The dip-slopes are covered with glacial till of local origin which is generally thin near the scarp edges and much thicker towards the centre of the plateaux (Fig. 7). The scarps are usually excessively drained, particularly near the top, where coarse quartz grit is generally exposed. Immediately

behind the scarp edge, where the drift is thin, free drainage is made possible by the proximity of the permeable sandstone below, but farther from the edge and wherever the till is thicker, drainage is very poor.

In the excessively drained position normal podzols occur; with free or slightly imperfect subsoil drainage, profiles develop which will be referred to here as 'thin iron-pan soils'; in the wettest positions deep peat forms above a deep grey gleyed subsoil (Fig. 8).

Normal podzols

On excessively drained sites immature podzolized soils occur. They have a peaty or mor humus surface overlying a somewhat bleached A_2 horizon with well-developed humus B_1 and iron B_2 horizons below. The iron B_2 horizon is always diffuse and is of the same order of thickness as the A_2 or B_1 horizons, and only rarely are there fragments of thin, hard, cemented, iron-pan discernible between the humus B_1 and the diffuse iron B_2.

Thin iron-pan soils (Fig. 9)

In the freely or slightly imperfectly drained position, particularly where shallow loamy textured till overlies a permeable sandstone, a very striking profile develops. A peat surface, from a few inches to several feet thick, overlies a dull brownish-grey horizon which merges into pale blue-grey gleyed loam or clay loam resting sharply on a thin continuous hard iron-pan rarely more than $\frac{1}{4}$ in. thick, which in turn rests upon yellow-brown freely drained, or at the most slightly imperfectly drained, C horizon. The thin iron-pan profiles vary greatly in depth and degree of development; generally the pan lies within 8 in. of the mineral surface, but it may be found deeper. A typical feature is the very erratic relative position of the thin iron-pan in the profile; from a general depth of about 8 in. below the mineral surface it may pitch downwards at some point to more than 2 ft. to rise again just as sharply only a few inches farther along. Peculiar contortions of this kind, and even completely separate iron-pan shells containing yellow-brown weathering material, are typical features of these profiles (cf. Muir and Fraser, 1940).

The iron-pan itself shows a consistent and striking morphology; even in the thinnest specimens the upper half is always shiny black and the lower half rusty-brown or liver-coloured. Immediately above the pan, remains of a root mat are always present. In the younger profiles the mat may be continuous, held together by active roots, but under deep peat the mat may be decomposed leaving only a film of greasy humus on the upper surface of the thin iron-pan.

It has been suggested (Muir, 1934; Stephens, 1950) that the thin iron-pan develops at the surface of the B_2 horizon of a normal podzol profile as a result of the impeding effect of the normal diffuse B horizon when it becomes indurated. The widespread occurrence of the 'walnut-shell layer' between the humus B and the iron B in many Scottish profiles (Muir, 1934; Ogg, 1935; Glentworth and Dion, 1949) and occasionally in the normal Lancashire podzols suggests that this process may sometimes occur, but there is ample evidence in Lancashire to show that this

is not always the explanation. In fields showing unmistakable evidence of ploughing, probably within the last 100 years, and now carrying very poor pasture, very shallow thin iron-pan profiles occur wholly within the previously cultivated layer. About 2 in. of an extremely acid peaty mat, often carrying much wavy hair grass (*Deschampsia flexuosa*), overlies about ½ in. to 1 in. of olive-grey bleached soil below which a sharp, very thin iron-pan is apparent. Beneath the iron-pan the profile is invariably freely or nearly freely drained. There is no sign whatever of the morphology of the normal podzol B horizon. Small areas are occasionally found, however, in which a second thin iron-pan occurs beneath the plough layer, presumably the remains of the original pan which was mostly destroyed by cultivation. The erratic variation in depth of the thin iron-pan in the deeper profiles described above is also typical of these 'micro-profiles' but to a much smaller degree.

It has also been suggested (Muir, 1934) that the thin iron-pan profiles develop as a result of the reduction of iron in a horizon of gleying immediately beneath the peaty surface due to the peat acting as a sponge and maintaining saturated conditions immediately below it. The iron, reduced in this horizon, oxidizes below through the agency of oxygen from the better drained lower part of the profile. The experiments by Bloomfield (1951) demonstrating the sorption of ferrous iron by ferric oxide suggest a mechanism by which this could occur.

The depth at which the thin iron-pan horizon occurs depends on many factors (Muir and Frazer, 1940), but from field evidence in Lancashire it seems likely that the profiles become deeper with increasing age, which involves a gradual deepening of each horizon so that the thin iron-pan moves downwards in the profile. Reduction and solution of iron on the upper surface of the pan could be followed by diffusion downwards through the pan with re-oxidation in the better aerated conditions on the underside. The better-developed pans appear to be so impervious that at first thought such a diffusion seems unlikely, but the existence of the thin iron-pan right through the centre of even fine-grained quartzite pebbles suggests that such movement is not impossible. Field evidence in support of this hypothesis is difficult to obtain; but the only alternative would be to regard the iron-pan as forming initially in the position in the profile where it is to remain, gradually increasing in thickness and impermeability. Although in some places under deep peat the thin iron-pan is within 3 or 4 in. of the mineral surface, it is often deeper than 1 ft. But the very young profiles which have developed on formerly cultivated land are *invariably* very shallow, with a very thin but persistent iron-pan often within 1 in. of the mineral surface. Occasionally a second iron-pan occurs below cultivation depth and presumably represents the remains of the more mature natural soil. Moreover, a downward movement of the iron-pan might provide an explanation for some of its peculiar contortions. Assuming reduction and oxidation to be the main processes in the development of the pan, the most intense and prolonged gleying might be expected in the shallow depressions occurring in the incipient pan, which would therefore, on the hypothesis of a downward movement, move downwards at a greater rate than the relatively higher parts of

the pan (Fig. 10). Thus, the more mature the profile, the greater the contortions to be expected, which seems to agree well with field observations.

Thin iron-pan profiles have not been observed in soils of very heavy texture. Occasionally, however, where thin peat overlies clay having an almost freely drained or imperfectly drained subsoil, a pale grey horizon underlies the peat, but below the pale grey horizon pronounced rusty or ochreous mottling often occurs on the structure faces, thus forming a zone of mottling rather than a continuous pan.

Peaty-gley soils

On upland sites with poor or very poor drainage peat 3 or 4 ft. deep is usual, and much greater depths are quite common. The upper layers of the peat are usually brown with fibrous or pseudo-fibrous structure, but towards the base it is generally more amorphous and the colour is darker, often nearly black. An inch or so of peaty loam often underlies the peat, and below this there is a drab brownish-grey horizon, usually about 8 in. thick, which merges downwards into pale grey loam or clay which shows a distinct greenish-blue tinge becoming more apparent with depth. The pale grey or bluish-grey colour on the surface of all the stones penetrates for some distance inwards, while many of the more porous rock fragments are grey or greenish-grey throughout and are relatively soft. In the wettest sites no mottling is visible, at least for a depth of several feet. However, in some situations, perhaps where waterlogging is not so continuous, or where better-drained horizons occur below the solum but within the reach of some roots, a very striking orange-coloured mottling occurs around dead root channels forming pipes of ferric oxide as described in the very poorly drained soils above.

Gley Features in other Major Soil Groups

Seasonal waterlogging is a feature of soils in many parts of the world, and it seems probable that some important morphological features in many of the Major Soil Groups are the result of gleying. The writer's experience of soils outside Britain is limited to a brief acquaintance with the soils of Australia and New Zealand, and the suggestions made in this part of the paper are therefore tentative.

Podzolic soils

In the zone of podzolic soils in Australia a catenary sequence can frequently be observed with Red Podzolic soils in positions of relatively good drainage, Yellow Podzolic soils in intermediate positions, and Grey Hydromorphic soils in the lowest sites. In the Yellow Podzolic soils particularly, features reminiscent of the gley soils described above are generally visible. A typical profile shows about 8 in. of greyish-brown sandy loam, merging into about 7 in. of pale brownish-grey sandy loam, passing sharply to mottled yellow and pale grey prismatic structured clay which becomes more yellow-brown or red and less pale grey with depth. The pale grey horizon and the mottled prismatic clay below form a pattern very like that in gley soils in Britain. Moreover, in the mottled horizon the pale grey is usually associated with structure faces and root

channels and presumably may be regarded as an extension of the pale grey horizon downwards along channels of moisture movement. Further confirmation that gleying is an important process in these podzolic soils may be found in the fact that water stands on the clay B horizon for considerable periods. In a profile examined outside Canberra, for instance, after a month's dry weather which had followed a period of heavy rain, water could be seen still seeping out of the A_2 horizon whilst the clay B horizon was relatively much drier.

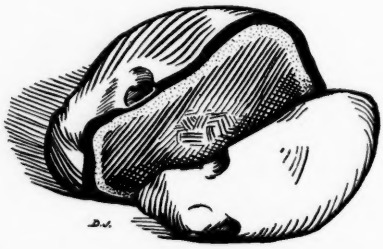

FIG. 11. Showing cross-section of a ferruginous concretion.

A very common but not universal feature of the A_2 horizon is the presence of numerous 'ironstone' nodules, often of very irregular shape. The nodules present some variety, but a section through one usually shows an outer shell of mainly ferric oxide surrounding a core of material often very like that in the B horizon, sometimes with a small hollow in the centre (Fig. 11). Examination of the outer shell shows that the outer half is shiny black and the inner half rusty or liver-coloured, exactly like the thin iron-pan described in the moorland soils above. It seems probable that ferrous iron mobilized during periods of waterlogging becomes re-oxidized during the dry season on the surface of some of the clods and gradually builds up a shell of ferric oxide (cf. Leeper, 1948). Such a process would perhaps be one explanation of the irregular 'nutty' shapes of many of the nodules which are rather reminiscent of some of the clods in gley soils. The occasional hollow centre might be explained by the drying of the nodule after the firm shell had been formed which would prevent any decrease in total volume, so that the clay inside would shrink, leaving a vesicular structure. A similar explanation has been advanced to explain some shrinkage effects in calcium carbonate nodules (Mitchell, 1951).

Some features in the Yellow-Grey Earths of New Zealand resemble those in the Podzolic soils of Australia. The pale grey mottling along the structure faces is almost certainly a result of reduction of iron during seasonal waterlogging, and it is likely, too, that the pale grey colour of the A_2 horizon results from the same cause. Soft ferruginous nodules occur in some soils in the A_2 horizon, and in a rather exceptional profile near Nelson (demonstrated by F. Chittenden, Cawthron Institute) hard ferruginous gravel above a clay B horizon presents an appearance exactly like that of many Australian Podzolic soils.

Laterites

There seems little doubt that laterites develop as a result of alternate seasonal waterlogging and drying under conditions of intense tropical weathering. In Australia, remains of laterite formed during the Pliocene period occur in most parts of the continent (Stephens, 1946), and many profile features are similar to features occurring in a very immature form in gley soils in Britain. The occurrence of a concretionary horizon over mottled and pale grey horizons is recognized to be, partly at least, a result of seasonal waterlogging with mobilization of iron followed by its oxidation in a concretionary zone. The general succession of horizons and the pattern of the mottling are often very like those in gleyed profiles.

The form of iron deposition in the concretionary zone varies, but pisolitic and nodular concretions are very common. They are variable in size and shape; the smaller nodules are often fairly smooth and rounded whilst the larger ones are more nutty. The smaller ones are often liver-coloured throughout, but the larger ones almost invariably show the iron oxide shell described above in connexion with the podzolic soils, and their genesis seems likely to be similar. In some profiles at least, the smaller nodules tend to be nearer the surface of the soil and give way gradually to larger ones below. If horizons may be regarded as moving downwards with the gradual lowering of the landscape it may be presumed that the small nodules nearest the surface are older than those below. It appears possible that some of them were originally larger iron-coated clods and that the ferric oxide shell, being attacked by reducing forces on the outside, gradually moved inwards until the whole mass of the small pebble became liver-coloured, which would be consistent with the observation that the smaller nodules usually contain the higher proportion of iron. The movement of the ferric oxide shell would thus be analogous to that suggested above for the downward movement of the iron-pan in British moorland soils.

Some New Zealand podzolized soils

Thin iron-pan soils can be seen in many parts of New Zealand. Probably the most extreme examples are the Pakihi soils of the Westport district (Harris, 1939) which occur under a well-distributed rainfall of more than 100 in. per annum, but well-developed thin iron-pans can also be seen under mainly Kamahi forest in Southland where depths of 2 ft. or more of Kamahi litter accumulate on the surface.

The Kauri tree (*Agathis australis*) of North Auckland often forms an even deeper litter which is extremely acid and causes intense podzolization with the development of an extremely siliceous A_2 horizon (Taylor *et al.*, 1950). On sandy parent materials well-developed thin iron-pan profiles occur in some situations, but in the heavier-textured profiles the rusty B horizons are thicker and laminated, sometimes almost giving the impression of a series of thin iron-pans, overlying the prismatic C horizons of yellow clay often mottled with pale grey. It is possible that the great depth of litter causes anaerobic conditions in the underlying mineral horizon and so produces gley phenomena resembling in some degree those in the British moorland thin iron-pan soils.

Solodized soils

In some of the solodized solonetz soils seen in the lower south-east of South Australia the rusty spotting in the bleached A_2 horizon and, in a few instances, the somewhat mottled appearance of the B horizon suggest gley phenomena. It is possible that the development of a pronounced texture profile leads to seasonal waterlogging above the clay B horizon and to mobilization of the iron in the ferrous condition.

Summary

Some morphological features of profiles showing various degrees of hydromorphism are described from soils under permanent pasture in north-west England. It is suggested that certain basic patterns are discernible in most gley soils, and the modifications resulting from variations in texture, structure, and position of the water-table in the profile are discussed.

A catenary sequence of soils including normal podzols, thin iron-pan soils, and peaty gley soils is described, and the development of the thin iron-pan considered.

It is suggested that the gleying process is responsible for some important features in other Major Soil Groups.

The colour pattern of some Australian Yellow Podzolic soils, and the development of ferruginous concretions in the A_2 horizon are related to gley phenomena. A similar explanation is advanced for certain morphological features of lateritic profiles.

Some New Zealand podzols are considered in relation to the thin iron-pan profiles.

It is suggested that mottling and rusty spotting in Solodic soils may be a result of gleying.

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REFERENCES

BALLS, W. L. 1951. Below soil level. Emp. Cott. Grow. Rev. **28**, 81.

BLOOMFIELD, C. 1951. Experiments on the mechanism of gley formation. J. Soil Sci. **2**, No. 2, 196.

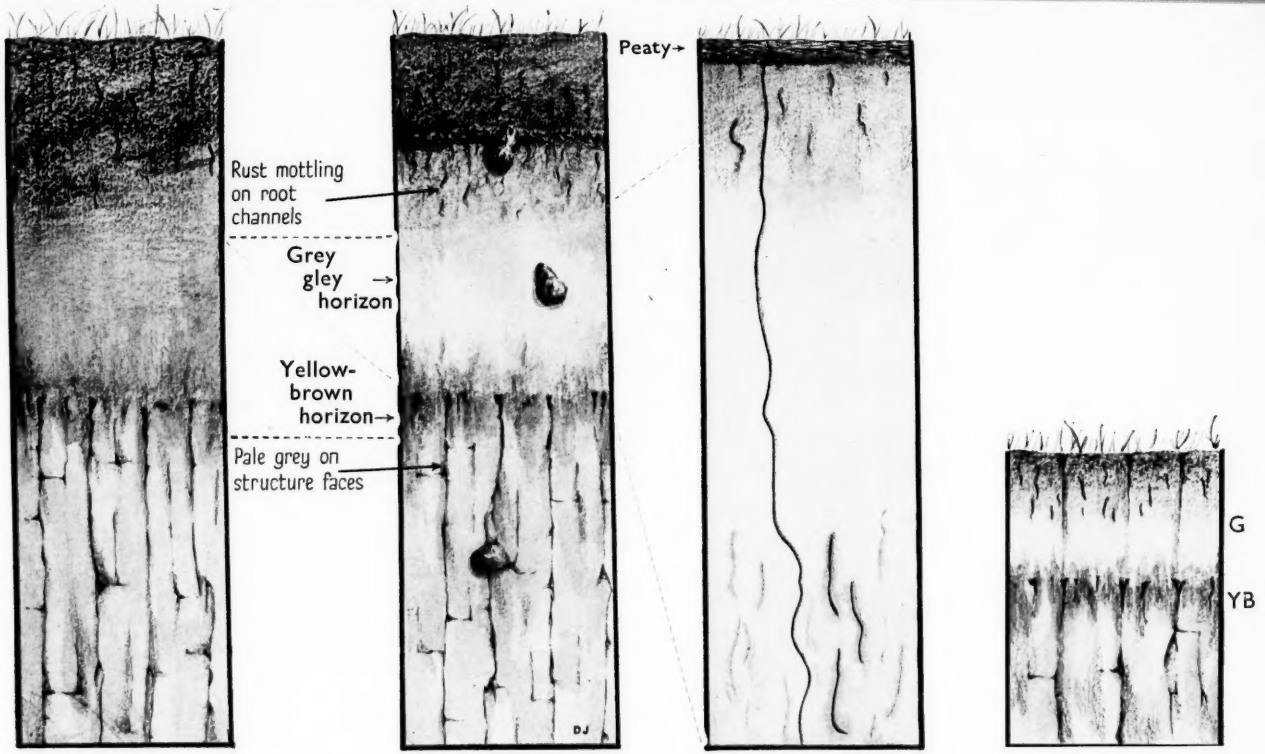
BUSHNELL, T. M. 1942. Some aspects of the soil catena concept. Proc. Soil Sci. Soc. Amer. **7**, 466.

—— 1944. The Story of Indiana Soils. Special Circular. Purdue Univ. Agric. Expt. Stn. Lafayette, Indiana.

—— 1948. Observations on hydrologic sequences in soils of America and Japan. Proc. Soil Sci. Soc. Amer. **13**, 481.

CLARKE, G. R. 1941. The Study of the Soil in the Field. O.U.P. 3rd edition.

DAVIES, W. M., and OWEN, G. 1934. Soil survey of north Shropshire. Emp. J. Expt. Agric. **2,** 6 and 8.
ELLIS, J. H. 1932. A field classification of soils for use in soil survey. Sc. Agric. **12,** 6.
FRASER, G. K. 1933. Studies of certain Scottish moorlands in relation to tree growth. Forestry Commission Bull. No. 15.
GLENTWORTH, R. 1944. Studies on the soils developed on basic igneous rocks in central Aberdeenshire. Trans. Roy. Soc. Edin. **61,** Pt. x, 1. 149.
—— and DION, N. G. 1949. The association or hydrologic sequence in certain soils of the Podzolic zone of north-east Scotland. J. Soil Sci. **1,** 35.
HARRIS, C. S., and HARRIS, A. C. 1939. Soil survey of Westport district. N.Z. D.S.I.R. Bulletin No. 71.
LACHAUSSÉE, E. 1950. Les sols sous la dominance de l'eau de la forêt. Rev. For. Franç. No. 5, 246.
LEEPER, G. W. 1948. Introduction to Soil Science. Melbourne Univ. Press.
MILNE, G. 1935. Some suggested units of classification and mapping particularly for East Africa. Soil Res. **4,** 183.
MITCHELL, W. A. 1951. Private communication.
MUIR, A. 1934. Soils of the Tiendland State Forest. Forestry, **8,** 25.
—— 1935. The soils of Drummond Hill. Ibid., **9,** 116.
—— and FRASER, G. K. 1940. The soils and vegetation of the Bin and Clashindarroch Forests. Trans. Roy. Soc. Edin. **60,** pt. 1, 233.
—— and BROWN, G. 1951. Private communication.
NICHOLSON, H. H. 1935. The drainage properties of heavy soils. Trans. 3rd Int. Cong. Soil Sci. **1,** 385.
OGG, W. G. 1935. The soils of Scotland. Emp. J. Expt. Agric. **3,** 174.
OTOTSKI, P., quoted by GLINKA, K. D. 1927. Dokuchaiev's ideas in the development of pedology and cognate sciences. Russian Pedological Investigations, U.S.S.R. Acad. of Sciences.
PEARSALL, W. H. 1950. Mountains and Moorlands. Collins.
STEPHENS, C. G. 1946. Pedogenesis following the dissection of lateritic regions in Southern Australia. Comm. Sc. Ind. Res. (Aust.) Bull. No. 206.
—— 1950. Comparative morphology and genetic relationships of certain Australian, North American, and European soils. J. Soil Sci. **1,** No. 2, 123.
TAYLOR, N. H., DIXON, J. K., and SEELYE, F. T. 1950. The soils of North Auckland Peninsula, New Zealand. Trans. 4th Int. Cong. Soil Sci. **1,** 293.

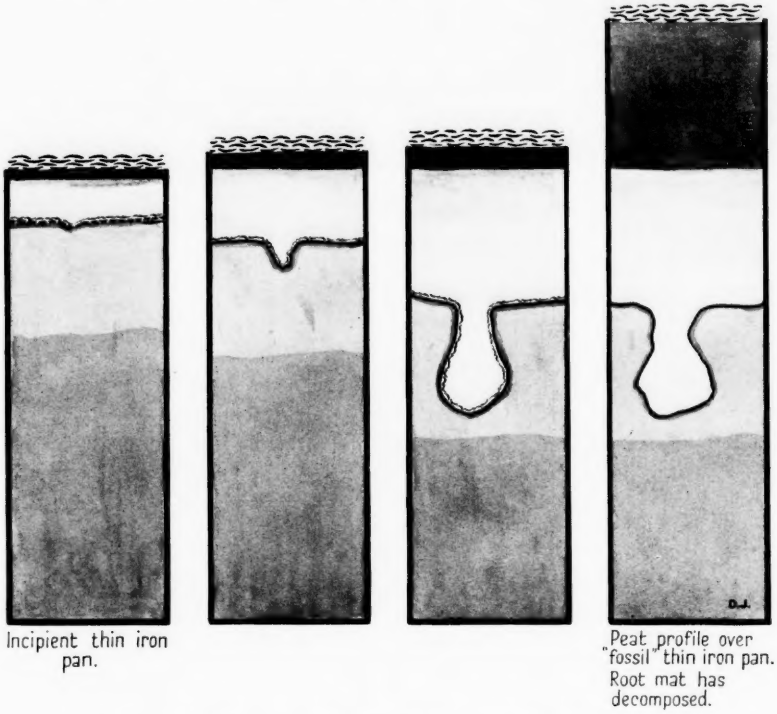


3. Slightly poorly drained profile

2. Poorly drained profile

4. Very poorly drained profile

5. Shallow, poorly drained profile in heavy clay



10. Possible development of thin iron-pan profiles

9. Thin iron-pan profile

9. Thin iron-pan profile